Technetium and Rhenium Complexes with Thioether Ligands, 5[◇]

Synthesis and Structural Characterization of Neutral Oxorhenium(V) Complexes with Tridentate Dithioethers

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Neutral oxorhenium(V) complexes of the general formula $ReO(L)Cl_2$ are obtained by reaction of $[ReO_4]^-$ or $[ReOCl_4]^-$ with functionalized dithiaalcohols (L) containing the donor atom sequences S, S, O^- and S, O^-, S. Ligand exchange reaction of $[ReOCl_4]^-$ with $HO(CH_2)_2S(CH_2)_2S(CH_2)_2OR$ (R = H, Et) leads to the formation of $ReOCl_2[O(CH_2)_2S(CH_2)_2S(CH_2)_2OH]$ (**1a**) and $ReOCl_2[O(CH_2)_2S(CH_2)_2S(CH_2)_2OEt]$ (**1b**). Reduction of $[ReO_4]^-$ with a 1:1 mixture of concentrated HCl and glacial acetic acid in the presence of nBuSCH$_2$-CH(OH)CH$_2$S–nBu yields $ReOCl_2[OCH(CH_2S-nBu)_2]$ (**4**). X-ray structure analysis of **1a**, **1b** and **4** shows distorted octahedral coordination with the chlorine and sulfur atoms in the equatorial plane. The oxygen of the hydroxyl group coordinates in a *trans* position with respect to the Re=O core. **1a** reacts with an excess of acetyl chloride in an unexpected way, resulting in cleavage of the *trans* Re–O bond and acylation of both of the hydroxyl groups to form the μ-oxo bridged complex $[ReOCl_2\{CH_3COO(CH_2)_2S(CH_2)_2S(CH_2)_2OOC-CH_3\}]_2O$ (**3**).

Introduction

Radionuclides of the group VII elements play an important role in nuclear medicine[2]. Diagnostic nuclear medicine relies heavily on the use of Tc-99m because of its nuclear properties[3], while Re-186 and Re-188 have nuclear properties suitable for therapeutic applications. There is a great potential for the use of various metals in radiopharmaceutical preparations, provided the environment around the metal is appropriately designed. Therefore there is a considerable search for chelating agents able not only to coordinate the metal in a definite manner but also to bear a pendant biological anchor group[4,5].

The potential of thioether ligands to coordinate technetium and rhenium in a stable and multidentate fashion has already been demonstrated[1,6]. Dithioether compounds used in this study offer advantages in two respects. Firstly, they combine the chelate unit with the functional group in the same ligand. Secondly, the radionuclide-containing part of the ligand remains relatively small. It is intended to keep the chelate part in the molecule as small as possible in order to minimize the alteration of the biomolecule.

In this paper we report on the reaction of functionalized dithiaalcohols as potential tridentate ligands with the oxorhenium(V) core. The syntheses and molecular structures of novel complexes containing the $[ReOCl_2S_2O]$ unit are described, as well as an acylation reaction leading to the binuclear product $[ReOCl_2\{CH_3COO(CH_2)_2S(CH_2)_2S-(CH_2)_2OOCCH_3\}]_2O$.

Results and Discussion

A general way of preparing rhenium complexes with thioether ligands is by ligand exchange reaction starting from a reactive precursor in organic solvents. In this way, reaction of the S,S,OH ligand 1,8-dihydroxy-3,6-dithiaoctane with $[AsPh_4][ReOCl_4]$ in methanol/acetone leads to the formation of the violet oxorhenium(V) complex $ReOCl_2[O(CH_2)_2S(CH_2)_2S(CH_2)_2OH]$ (**1a**). The neutral compound can be isolated as crystals suitable for X-ray analysis by slow evaporation of the solvents. In the same way, 1-hydroxy-3,6-dithia-9-oxaundecane reacts with the above precursor to afford violet crystals of $ReOCl_2-[O(CH_2)_2S(CH_2)_2S(CH_2)_2OEt]$ (**1b**). In the infrared spectra a strong absorption band at 940 cm^{-1} (for **1a**) and 948 cm^{-1} (for **1b**) is indicative of the $Re{=}O^{3+}$ core. The ^{1}H-NMR spectra of **1a** and **1b** show numerous multiplets for the methylene protons. Additionally, a triplet (δ = 1.19) and a quartet (δ = 3.58) are observed for the ethyl group of **1b**.

The molecular structure of **1a** is shown in Figure 1. Selected bond lengths and angles are compiled in Table 2.

In **1a** the rhenium atom is centred in a distorted octahedron with the equatorial plane formed by an S_2Cl_2 donor set. The oxygen atom of one of the terminal hydroxyl groups coordinates in a *trans* position with regard to the Re=O core. The second hydroxyl group remains noncoordi-

[◇] Part 4 see ref.[1].

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Scheme 1

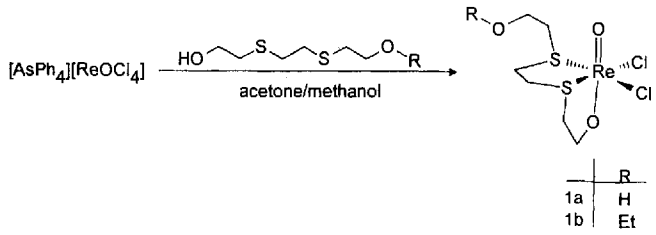
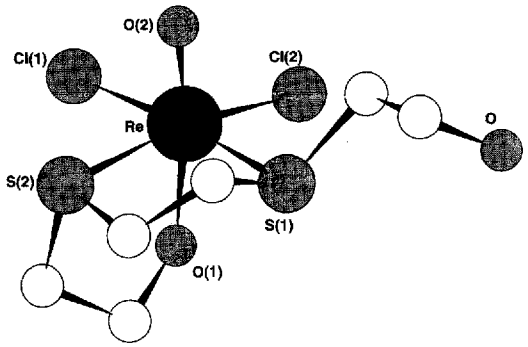


Figure 1. Molecular structure of dichloro[8-hydroxy-3,6-dithiaoctan-2-olato(O,S,S)]oxorhenium(V) **1a**



nated and offers an ideal site for further functionalization.

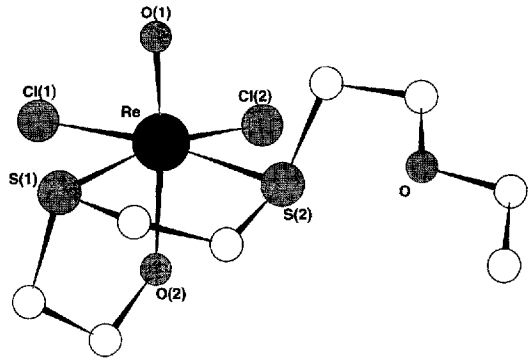
The great spatial requirement of the chlorines leads to a reduction of the O–Re–O angle from 180° in the regular octahedron to 164.8(8)°. The Re–O(2) bond length of 1.71(2) Å is comparable with that of the equivalent O–Re bond in analogous complexes containing the O=Re–O unit[7]. This is also true for the Re–O(1) distance of 1.92(2) Å. The Re–S distances of 2.428–2.439 Å are in the expected range[8].

The *trans*-position to the double bonded oxygen is known to be labile. Investigations of a possible substitution of the coordinated hydroxyl group by protic solvents have been carried out by UV/Vis spectroscopy. The spectra of both **1a** and **1b** show weak absorption bands at 371 nm and 522 nm in the aprotic solvent DMF. Addition of methanol does not cause a shift in these bands, i.e. there is no evidence for a displacement of the hydroxyl group by a protic solvent molecule.

As illustrated in Figure 2 and Table 2 the structural data of **1b** are equivalent to those of **1a** with the exception of the terminal ethyl group.

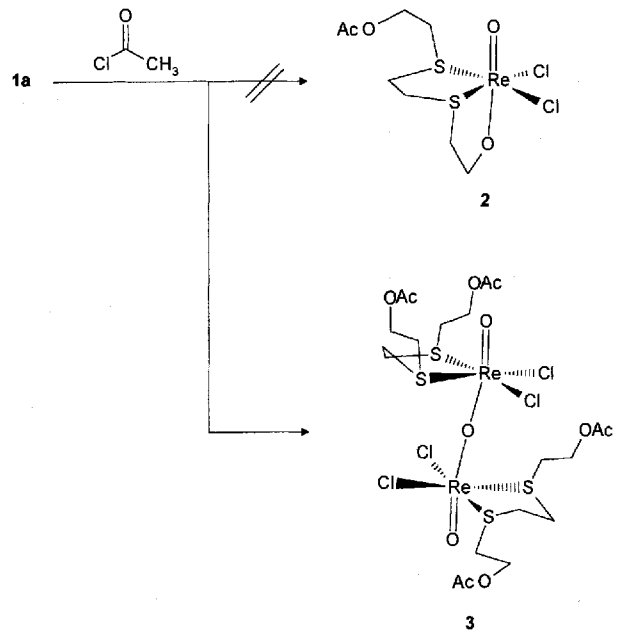
In order to investigate the possibilities of further derivatization at the noncoordinated hydroxyl group in **1a**, a typical acylation reaction was studied. Considering the conditions prevailing in radiopharmaceutical preparations, in particular the great excess of other species with respect to the low metal concentration, an excess of acetyl chloride was added to complex **1a**. Instead of the expected monoester **2**, the reaction led to cleavage of the *trans* Re–O bond and subsequently to esterification of both of the hydroxyl groups, forming the μ-oxo bridged complex **3**. During the course of the reaction the colour changed from violet to turquoise-green (see Scheme 2). In the infrared spectrum of

Figure 2. Molecular structure of dichloro[3,6-dithia-9-oxaundecan-1-olato(O,S,S)]oxorhenium(V) **1b**



the product, strong vibrational bands at 696 and 668 cm^{-1} could be observed, indicative of an O=Re–O–Re=O core. The ^{1}H-NMR spectrum showed multiplets due to the methylene protons and a singlet at δ = 2.14 due to the methyl group.

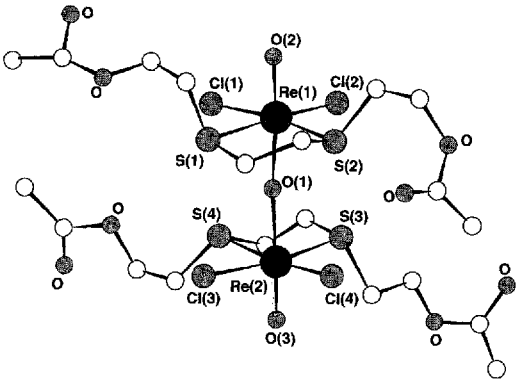
Scheme 2



Dark-green crystals of **3** suitable for X-ray analysis were obtained from the reaction mixture by slow evaporation of the excess acetyl chloride. The molecular structure of **3** is illustrated in Figure 3. The axis of the molecule is formed by the O=Re–O–Re=O moiety, which shows a significant deviation from linearity [angle O=Re–O = 174.0(1)°].

The chlorine and sulfur atoms are positioned at the corners of the equatorial planes. With respect to the bridging oxygen, the chlorines and bidentate ligands are placed in an *anti* position. A view parallel to the Re···Re vector shows that the chlorines of one $ReOCl_2S_2$ unit almost eclipse the sulfur atoms of the other part of the molecule (torsion angle Cl–Re–Re–S: 2.4–5.4°). The bond lengths and angles of **3** (see Table 2) are in agreement with previous observations[1].

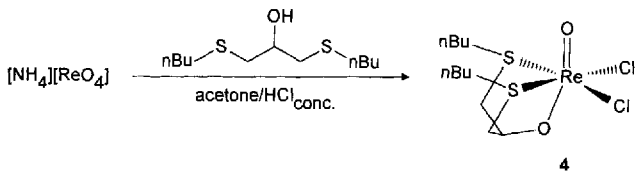
Figure 3. Molecular structure of μ-oxobis{dichloro[1,8-diacetoxy-3,6-dithia-octane(S,S)]oxorhenium(V)} **3**



Equivalent complexes of the general composition $[MO(L_4)]_2(\mu\text{-}O)$ (L_4 = tetradentate, two bidentate, bidentate and two monodentate or four monodentate ligands, M = Mo, Re, Tc) have been intensively studied[9]. The basic structure of these compounds is formed by two independent metal-centred octahedra with a common corner occupied by an oxygen.

The dithioether nBuSCH$_2$CH(OH)CH$_2$S–nBu, containing the S, O, S donor sequence, reacted in a similar manner to the dithiaalcohols bearing a terminal hydroxyl group. Reduction of $[NH_4][ReO_4]$ with a 1:1 mixture of concentrated HCl and glacial acetic acid in the presence of an excess of the ligand afforded complex **4**. In this reaction $[ReOCl_4]^-$ can be assumed as an intermediate (see Scheme 3). A violet solid precipitated from the reaction mixture within a few minutes. Recrystallization from chloroform/diethyl ether yielded violet crystals suitable for X-ray analysis. The infrared spectrum and the NMR spectra support the structure of **4**.

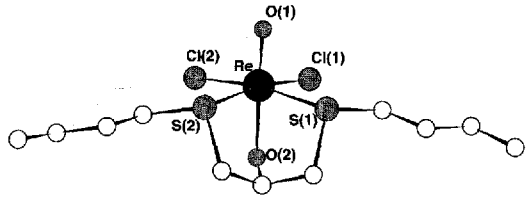
Scheme 3



The X-ray crystal structure of **4** shows a strongly distorted O(1), O(2), S(1), S(2), Cl(1), Cl(2) octahedron (Figure 4). Apart from the space-filling properties of the chlorine atoms, the ring strain of the bicyclo[2.2.1]ReC_3S_2O is assumed to be the main reason for the strong decrease of the O=Re–O angle [157.8(4)°]. The metal atom is slightly displaced from the S_2Cl_2 plane towards the apical O atom by 0.198 Å (Table 2).

In conclusion, it can be said that the complexes presented here possess a compact structure, which is a favourable property in the development of Tc-99m radiopharmaceuticals. The advantage of these molecules is that there is only one position on the ligand at which further functionalization can be carried out. Unfortunately the acylation reaction is not restricted to the non-coordinated hydroxyl group.

Figure 4. Molecular structure of dichloro[5,9-dithiatridecan-7-olato-(O,S,S)]-oxorhenium(V) **4**



Besides the hydroxyl groups, the chlorine atoms in these systems also present potential sites for substitution. This will be the subject of a further publication.

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Experimental Section

General: All solvents and commercially available substances such as $[NH]_4[ReO_4]$ and 1,8-dihydroxy-3,6-dithiaoctane were of analytical grade. $[AsPh_4][ReOCl_4]$ was prepared according to a literature procedure[10]. – IR: Specord M 80 Carl-Zeiss Jena. – UV/Vis: Specord S10 Carl-Zeiss Jena. – NMR: Bruker 500 MHz, TMS as internal standard.

X-ray Crystallographic Study[11]: The X-ray data were collected at room temperature (296 K) on an Enraf-Nonius CAD 4 diffractometer, using graphite monochromated Mo-K_α radiation (λ = 0.71073 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 and refined anisotropically. Subsequently, the hydrogen positions were calculated according to ideal geometries. Absorption corrections with the program DIFABS[12] were made at two stages during the structure refinement. Most of the calculations were carried out in the Enraf-Nonius SDP system with some local modifications.

Table 1. Crystal structure parameters of complexes **1a**, **1b**, **3** and **4**

	1a	**1b**	**3**	**4**
Emp. formula	$C_6H_{12}Cl_2O_3ReS_2$	$C_8H_{17}Cl_2O_2ReS_2$	$C_{20}H_{36}Cl_4O_{11}Re_2S_4$	$C_{11}H_{23}Cl_2O_2ReS_2$
Form. weight	454.38	482.44	1094.93	508
Cryst. system	orthorhombic	monoclinic	orthorhombic	orthorhombic
Space group	*Pbca*	$P2_1/n$	$Pna2_1$	$P2_12_12_1$
a [Å]	8.086(4)	7.215(4)	17.135(4)	7.9045(2)
b [Å]	11.218(7)	16.845(6)	8.527(2)	9.5736(3)
c [Å]	27.162(7)	12.119(2)	23.344(9)	23.2455(2)
α [°]	90.00	90.00	90.00	90.00
β [°]	90.00	99.37(3)	90.00	90.00
γ [°]	90.00	90.00	90.00	90.00
Volume [Å^3]	2464(2)	1453.3(10)	3411(2)	1759.09
Z	8	4	4	4
Temp. [K]	293(2)	293(2)	293(2)	296
δ [g/cm^3]	2.450	2.205	2.132	1.920
Abs. coeff. [mm^{-1}]	10.616	9.006	7.700	7.442
F(000)	1712	920	2104	984
μ(Mo-K_α) [Å]	0.71070	0.71069	0.71070	0.71073
Cryst. size [mm^3]	0.54 × 0.36 × 0.04	0.31 × 0.18 × 0.11	0.55 × 0.36 × 0.11	0.36 × 0.18 × 0.03
θ range	1.50–24.96	2.09–24.97	1.74–24.97	2.3–27.5
Index ranges	$0 \le h \le 9$	$0 \le h \le 8$	$0 \le h \le 20$	$-10 \le h \le 12$
	$0 \le k \le 13$	$0 \le k \le 20$	$0 \le k \le 10$	$-7 \le k \le 14$
	$0 \le l \le 22$	$-14 \le l \le 14$	$-27 \le j \le 0$	$-11 \le j \le 35$
Refins. collected	1880	2768	2503	7050
Indep. refins.	1880	2556	2503	3884
GOF on F^2	1.161	1.041	1.080	1.145
Final *R* indices	$R1 = 0.0689$	$R1 = 0.0304$	$R1 = 0.0732$	$R1 = 0.0563$
[$I > 2\sigma(I)$]	$wR2 = 0.1861$	$wR2 = 0.0720$	$wR2 = 0.1974$	$wR2 = 0.1079$
R indices	$R1 = 0.0882$	$R1 = 0.0499$	$R1 = 0.0732$	$R1 = 0.0758$
(all data)	$wR2 = 0.1969$	$wR2 = 0.0794$	$wR2 = 0.1974$	$wR2 = 0.1219$
Largest diff. peak	1.789	1.130	3.834	1.307
Largest diff. hole	–1.241	–0735	–4.285	–0.991

For complex **3** only crystals of rather poor quality were available (all crystals consisted of more than two pieces). This explains the relatively large values for the "largest difference peak" and the "largest difference hole". The assignment of the enantiomers of complexes **3** and **4** to the structures presented was made on the basis of the Flack parameter[13] (for **3**: 0.3; for **4**: 0.02).

Relevant bond lengths and angles are summarized in Table 2. Atomic positional and thermal parameters, full lists of bond lengths and angles, and F_o/F_c values have been deposited as supplementary material[11].

Table 2. Selected bond lengths and angles of complexes **1a**, **1b**, **3** and **4**

1a					
Re–Cl(1)	2.437 (6)	Re–S(1)	2.428 (6)	Re–O(1)	1.92 (2)
Re–Cl(2)	2.388 (6)	Re–S(2)	2.439 (7)	Re–O(2)	1.71 (2)
Cl(1)–Re–Cl(2)	90.2 (2)	Cl(2)–Re–S(1)	94.1 (2)	S(1)–Re–O(1)	86.1 (5)
Cl(1)–Re–S(1)	174.4 (2)	Cl(2)–Re–S(2)	168.5 (3)	S(1)–Re–O(2)	88.0 (7)
Cl(1)–Re–S(2)	90.1 (2)	Cl(2)–Re–O(1)	89.9 (5)	S(2)–Re–O(1)	78.6 (5)
Cl(1)–Re–O(1)	90.5 (5)	Cl(2)–Re–O(2)	104.5 (7)	S(2)–Re–O(2)	86.9 (7)
Cl(1)–Re–O(2)	94.2 (7)	S(1)–Re–S(2)	84.9 (2)	O(1)–Re–O(2)	164.8(8)
1b					
Re–Cl(1)	2.405 (3)	Re–S(1)	2.428 (2)	Re–O(1)	1.686(6)
Re–Cl(2)	2.360 (3)	Re–S(2)	2.422 (3)	Re–O(2)	1.917 6)
Cl(1)–Re–Cl(2)	91.2 (1)	Cl(2)–Re–S(1)	168.2 (1)	S(1)–Re–O(1)	88.3(2)
Cl(1)–Re–S(1)	90.74 (9)	Cl(2)–Re–S(2)	90.03 (9)	S(1)–Re–O(2)	78.8(2)
Cl(1)–Re–S(2)	172.6 (1)	Cl(2)–Re–O(1)	103.2 (2)	S(2)–Re–O(1)	92.4(2)
Cl(1)–Re–O(1)	94.4 (2)	Cl(2)–Re–O(2)	89.5 (2)	S(2)–Re–O(2)	83.0(2)
Cl(1)–Re–O(2)	89.7 (2)	S(1)–Re–S(2)	86.59 (2)	O(1)–Re–O(2)	166.5(3)
4					
Re–Cl(1)	2.370 (4)	Re–S(1)	2.482 (3)	Re–O(1)	1.692(9)
Re–Cl(2)	2.363 (4)	Re–S(2)	2.462 (3)	Re–O(2)	1.953(8)
Cl(1)–Re–Cl(2)	85.8 (2)	Cl(2)–Re–S(1)	170.26 (13)	S(1)–Re–O(1)	86.3 3)
Cl(1)–Re–S(1)	93.04 (13)	Cl(2)–Re–S(2)	93.34 (13)	S(1)–Re–O(2)	77.7(3)
Cl(1)–Re–S(2)	170.49 (13)	Cl(2)–Re–O(1)	92.7 (3)	S(2)–Re–O(1)	86.4(3)
Cl(1)–Re–O(1)	93.3 (3)	Cl(2)–Re–O(2)	103.4 (4)	S(2)–Re–O(2)	77.3(3)
Cl(1)–Re–O(2)	103.0 (3)	S(1)–Re–S(2)	86.21 (11)	O(1)–Re–O(2)	157.8(4)
3					
Re(1)–Cl(1)	2.505 (9)	Re(1)–O(2)	1.72 (2)	Re(2)–S(3)	2.40(1)
Re(1)–Cl(2)	2.359 (9)	Re(2)–O(2)	1.72 (1)	Re(2)–S(4)	2.46(1)
Re(1)–S(1)	2.51 (1)	Re(2)–Cl(3)	2.47 (1)	Re(2)–O(1)	1.97(2)
Re(1)–S(2)	2.35 (1)	Re(2)–Cl(4)	2.36 (1)	Re(2)–O(3)	1.67(2)
Re(1)–O(1)	1.88 (2)				
Cl(1)–Re(1)–Cl(2)		S(1)–Re(1)–O(1)		Cl(4)–Re(2)–S(3)	
Cl(1)–Re(1)–S(1)	90.3 (3)	S(1)–Re(1)–O(2)		Cl(4)–Re(2)–S(4)	
Cl(1)–Re(1)–S(2)	172.3 (3)	S(2)–Re(1)–O(1)		Cl(4)–Re(2)–O(1)	
Cl(1)–Re(1)–O(1)		S(2)–Re(1)–O(2)		Cl(4)–Re(2)–O(3)	
Cl(1)–Re(1)–O(2)		O(1)–Re(1)–O(2)		S(3)–Re(2)–S(4)	
Cl(2)–Re(1)–S(1)	175.9 (3)	Cl(3)–Re(2)–Cl(4)		S(3)–Re(2)–O(1)	
Cl(2)–Re(1)–S(2)	94.3 (3)	Cl(3)–Re(2)–S(3)		S(3)–Re(2)–O(3)	
Cl(2)–Re(1)–O(1)		Cl(3)–Re(2)–S(4)		S(4)–Re(2)–O(1)	
Cl(2)–Re(1)–O(2)		Cl(3)–Re(2)–O(1)		S(4)–Re(2)–O(3)	
S(1)–Re(1)–S(2)	86.1 (3)	Cl(3)–Re(2)–O(3)		O(1)–Re(2)–O(3)	
Re(1)–O(1)–Re(2)					

Dichloro[8-hydroxy-3,6-dithiaoctan-1-olato-(O^1,S,S)]oxorhenium(V) (**1a**) *and Dichloro[3,6-dithia-9-oxaundecan-1-olato-(O^1,S,S)]oxorhenium(V)* (**1b**): To 100 mg (137 μmol) of $[AsPh_4][ReOCl_4]$, dissolved in 2 ml of acetone, a solution of 200 μmol of 1,8-dihydroxy-3,6-dithiaoctane (for **1a**) or 1-hydroxy-3,6-dithia-9-oxaundecan-1-ol (for **1b**)[14], dissolved in 1 ml of acetone, was added. After addition of 2 ml of methanol the reaction mixture was stirred for 1 h at room temperature. Slow evaporation of the reaction mixture yielded violet crystals suitable for X-ray analysis. – **1a**: Yield: 46 mg (73%), m.p. 144–146°C. – IR (KBr): $\tilde{\nu}$ = 1072 cm^{-1} (C–O), 940 (Re=O), 524 (Re–O). – UV ($CHCl_3$): λ_{max} (ε) = 371 nm (235), 522 (128). – ^1H NMR ([D$_7$]DMF): The complex spectrum could not be assigned because of the peak broadening and superposition. – ^{13}C NMR ([D$_7$]DMF): δ = 40.30, 41.62, 46.88, 49.13, 60.24 ($HOCH_2CH_2S$), 72.39 ($ReOCH_2$). – $C_6H_{13}Cl_2O_3ReS_2$ (454): calcd. C 15.86, H 2.88, S 14.11, Cl 15.60; found C 16.07, H 2.91, S 14.23, Cl 15.52. – **1b**: Yield: 61 mg (92%), m.p. 158–160°C. – IR (KBr): $\tilde{\nu}$ = 1120 cm^{-1} (C–O), 1076 (C–O), 948 (Re=O), 520 (Re–O). – UV ($CHCl_3$): λ_{max} (ε) = 372 nm (235), 522 (98). – ^1H NMR ([D$_7$]DMF): δ = 1.19 (t, J = 6.9 Hz, 3H, CH_3CH_2), 3.58 (q, J = 6.9 Hz, 2H, CH_3CH_2), the methylene region of the spectrum was too complex to be analysed. – ^{13}C NMR ([D$_7$]DMF): δ = 15.26 ($CH_3CH_2OCH_2$), 40.24, 41.73, 44.00, 49.14, 66.57 ($CH_3CH_2OCH_2$), 68.23 ($CH_3CH_2OCH_2$), 73.87 ($ReOCH_2$). – $C_8H_{17}Cl_2O_3ReS_2$ (482): calcd. C 19.92, H 3.52, S 13.28, Cl 14.73; found C 20.12, H 3.55, S 13.18, Cl 14.73.

μ-Oxobis{dichloro[1,8-diacetoxy-3,6-dithiaoctane(S,S)]-oxorhenium(V)} (**3**): 30 mg (66 μmol) of **1a** was stirred in 3 ml of acetyl chloride for 2 h at room temperature. Within this time the complex dissolved and the colour changed from violet to turquoise. Slow evaporation of the excess acetyl chloride yielded dark-green crystals suitable for X-ray analysis. – Yield: 65 mg (90%), 187–189°C. – IR (KBr): $\tilde{\nu}$ = 1740 cm^{-1} (C=O), 1228 (C–O), 696, 668 (O=Re–O–Re=O). – UV (CH_3CN): λ_{max} (ε) = 304 nm (11890). – ^1H NMR (CD_3CN): δ = 2.14 (s, 12H,CH_3), 2.33 (m, 16H, SCH_2CH_2S), 3.5–4.5 (m, 32H, SCH_2CH_2OCO). – ^{13}C NMR (CD_3CN): δ = 21.02 (CH_3), 31.08 and 32.98 (CH_2SCH_2), 64.40 (CH_2O), 171.45 (C=O). – $C_{20}H_{36}Cl_4O_{11}Re_2S_4$ (1094): calcd. C 21.94, H 3.29, S 11.70, Cl 12.98; found C 21.66, H 3.18, S 11.52, Cl 13.23.

Dichloro[5,9-dithiatridecan-7-olato-(O,S,S)]oxorhenium(V) (**4**): To 40.2 mg (150 μmol) of $[NH_4][ReO_4]$, dissolved in 1.5 ml of concentrated HCl, 47.3 mg (200 μmol) of 5,9-dithiatridecan-7-ol[15], dissolved in 1 ml of glacial acetic acid, was added. After 20 min a violet precipitate was filtered off and washed three times with glacial acetic acid and then three times with diethyl ether. Crystals suitable for X-ray analysis were obtained by recrystallization from $CHCl_3$/diethyl ether. Yield: 53 mg (69%), 128–129°C. – IR (KBr): $\tilde{\nu}$ = 1040 cm^{-1} (C–O), 960 (Re=O), 532 (Re–O). – UV ($CHCl_3$): λ_{max} (ε) = 373 nm (106), 522 (102). – ^1H NMR ($CDCl_3$): δ = 0.97 (t, ^3J = 7.2 Hz, 6H, CH_3), 1.54 (m, ^3J = 7.2 Hz, 4H, $CH_2CH_2CH_2CH_3$), 1.75–1.90 (m, 4H, $CH_2CH_2CH_2CH_3$), 2.60 (dd, ^2J = 12.6, ^3J = 6.1 Hz, 2H, SCH_2CHO), 2.86 (d, ^2J = 12.6, 2H, SCH_2CHO), 2.98 (ddd, ^2J = 12.3, ^3J = 6.1, ^3J = 6.0 Hz, 2H, $CH_2CH_2CH_2CH_3$), 3.58 (ddd, ^2J = 12.3, ^3J = 6.1, ^3J = 6.0 Hz, 2H, $CH_2CH_2CH_2CH_3$), 6.08 (d, ^3J = 6.1 Hz, 1H, C–H). – ^{13}C NMR ($CDCl_3$): δ = 13.96 ($CH_3CH_2CH_2CH_2S$), 21.95 ($CH_3CH_2CH_2CH_2S$), 29.11 ($CH_3CH_2CH_2CH_2S$), 42.31 ($CH_3CH_2CH_2CH_2S$), 44.53 (SCH_2CHO), 84.60 (CHO). – $C_{11}H_{23}Cl_2O_2ReS_2$ (508): calcd. C 25.98, H 4.56, S 12.61, Cl 13.94; found C 25.44, H 4.44, S 12.31, Cl 13.81.

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