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TECHNETIUM AND RHENIUM COMPLEXES WITH THIOETHER LIGANDS—IV.* SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF BINUCLEAR OXORHENIUM(V) COMPLEXES WITH BIDENTATE THIOETHER COORDINATION

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Abstract—Binuclear oxorhenium(V) complexes, [ReO(“S_2”)Cl_2]$_2$O, have been prepared by reduction of ReO_4^- with $SnCl_2$ in strongly acidic solution and in the presence of aliphatic thioethers of the general formula R—CH_2CH_2—S—CH_2CH_2—S—CH_2CH_2—R′ (“S_2”; R, R′ = H, Et; R = S—Bu, R′ = Et; R = O—Et, R′ = H; R, R′ = O—Et). Alternatively the compounds can be obtained by ligand exchange reactions starting from $[ReOCl_4]^-$ in methanolic solution. A representative derived from 5,8-dithiadodecane (R,R′ = Et) has been studied by X-ray diffraction. The complex consists of two independent [ReO(“S_2”)Cl_2] units bridged by an oxygen atom. Each rhenium atom is centred in a distorted octahedron with the equatorial plane formed by the S_2Cl_2 donor set. The sulphur and chlorine atoms of the units are in the *anti* position with respect to the bridging oxygen.

Recently we described the synthesis and characterization of a novel class of neutral binuclear oxotechnetium(V) complexes, [TcO(“S_2”)Cl_2]$_2$O.[1,2]

The compounds, which can be obtained by ligand exchange reactions of $[TcOCl_4]^-$ with bidentate thioethers (“S_2”), are of interest as potential tracers for radiodiagnostic application.

Because rhenium nuclides ^{186}Re and ^{188}Re emit β-particles with therapeutically useful energies, rhenium is included in our efforts to evaluate novel thioether complexes as tracers for radiotherapeutic purposes.

The present paper reports on the synthesis and structure of μ-oxo bridged oxorhenium(V) complexes with mixed bidentate thioether/chlorine coordination.

EXPERIMENTAL

UV–vis spectra were recorded on a Specord UV/VIS S10 spectrometer from Zeiss Germany with DMF (complex **1**) and chloroform (**2**–**5**) as solvents.

IR spectra were measured as KBr discs on a Specord M 80 spectrometer from Carl Zeiss Jena.

NMR spectra were recorded on a Bruker WH 90 instrument using TMS as internal reference and DMSO (complex **1**) and chloroform (**2**–**5**) as solvents.

Syntheses

NH_4ReO_4 was purchased from Aldrich Chem.

$AsPh_4[ReOCl_4]$ was prepared by the method

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* For Part III see ref. 1.

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described previously[3] with some modifications. The ligands were synthesized according to Feher and Vogelbruch.[4]

All manipulations were performed under argon using standard Schlenk and vacuum-line.

General procedure for the preparation of **1–5** *by reduction of* ReO_4^-

Thioether (375 μmol) dissolved in acetone (2 cm^3) was added to a stirred solution of NH_4ReO_4 (40.2 mg, 150 μmol) in acetone/5 N HCl (1/1, 3 cm^3). After addition of $SnCl_2 \cdot 2H_2O$ (41 mg, 180 μmol) dissolved in 5 N HCl (1/cm^3) the colour changed from white to blue–green and a turquoise powder precipitated. The complex was filtered off and washed first with methanol and then with diethyl ether. Recrystallization from chloroform/diethyl ether gave green crystals. Yields were between 65% and 70%.

General procedure for the preparation of **1–5** *by ligand exchange reactions*

Thioether (375 μmol) dissolved in acetone (1 cm^3) was added to $AsPh_4[ReOCl_4]$ (109 mg, 150 μmol) dissolved in acetone (2 cm^3). After addition of methanol (3 cm^3) the mixture was stirred for 1 h. During this time colour changed from yellow to blue–green and a turquoise powder precipitated. The complexes were worked up as described above. Yields were between 70% and 80%.

Crystals of complex **2** suitable for X-ray analysis were obtained by slow evaporation of a chloroform/methanol solution.

Structure determination and crystal data

The X-ray data were collected at room temperature (296 K) on an Enraf-Nonius CAD 4 diffractometer, using graphite monochromatized Mo-K_α radiation ($\lambda = 0.71073$ 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. 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 the structure refinement. Most of the calculations were carried out in the Enraf-Nonius SDP system with some local modifications. Relevant bond lengths and angles are contained 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.

Table 1. Experimental crystallographic data for $[ReO(5,8\text{-dithiadodecane})_2Cl_2]_2O$ (**2**)

Molecular formula	$C_{20}H_{44}O_3S_4Cl_4Re_2$
Molecular weight	975.03
Crystal system	Orthorombic
Space group; No.	*Pbca*; 61
a (Å)	16.5910(8)
b (Å)	17.1980(7)
d (Å)	23.6050(9)
V (Å^3)	6735.3
Z; $F(000)$; d_{calc} (g cm^{-3})	8; 3760; 1.923
T(K)	296
Data collection	
Crystal size (mm^3)	$0.72 \times 0.18 \times 0.05$
λ (Mo-K_α Å)	0.71073
μ (cm^{-1})	78.611
Data sphere (°)	$3 < 2\Theta \leqslant 44$
Scan mode	$\omega - 2\Theta$
Scan rate ° min^{-1}	variab. 1.5–4.8
Miller ind. range	h 0–17 k 0–18 l 0–24
Unique refl. meas.	4112
Unique refl. used [$I_o \geqslant 3\sigma(I)$]	2950
Check reflections	6 −6 −5 0 −12 1 0 −8 7
Absorpt. correct.	Yes
$R = \dfrac{\Sigma[\lvert F_o\rvert - \lvert F_c\rvert]}{\Sigma[\lvert F_o\rvert]}$	0.050

RESULTS AND DISCUSSION

The reduction of ReO_4^- by stannous chloride in strongly acidic solution and in the presence of aliphatic thioethers containing the —S—CH_2 CH_2—S— moiety leads to the formation of neutral complexes with mixed bidentate thioether/chlorine coordination.

According to elemental analysis, compounds **1**–**5** were found to be binuclear oxorhenium(V) complexes of the general formula $[ReO(\text{“}S_2\text{”})Cl_2]_2O$ (“S_2” = thioether; Fig. 1 and Table 3).

The same compounds are obtained by ligand exchange reactions starting from $[ReOCl_4]^-$ with an excess of the ligand in methanolic solution.

Obviously the *cis*-$ReOS_2Cl_2$ moiety seems to be the favoured unit. This follows from the facts that on the one hand the ligand exchange reaction proceeds only with a partial exchange of the chloride ligands by two S atoms of the thioether and on

Table 2. Selected bond lengths (Å) and angles (°) for [ReO(5,8-dithiadodecane)$_2$Cl$_2$]$_2$ O (**2**)

Re(1)—Cl(1)	2.405(2)	Re(2)—Cl(3)	2.401(2)
Re(1)—Cl(2)	2.395(2)	Re(2)—Cl(4)	2.395(2)
Re(1)—S(1)	2.439(2)	Re(2)—S(3)	2.419(2)
Re(1)—S(2)	2.410(2)	Re(2)—S(4)	2.420(2)
Re(1)—O(1)	1.705(8)	Re(2)—O(2)	1.735(4)
Re(1)—O(3)	1.908(9)	Re(2)—O(3)	1.946(9)

Cl(1)—Re(1)—Cl(2)	89.53(7)	Cl(3)—Re(2)—Cl(4)	89.63(9)
Cl(1)—Re(1)—S(1)	91.27(7)	Cl(3)—Re(2)—S(3)	93.10(9)
Cl(1)—Re(1)—S(2)	173.82(6)	Cl(3)—Re(2)—S(4)	173.36(7)
Cl(1)—Re(1)—O(1)	100.7(3)	Cl(3)—Re(2)—O(2)	93.8(3)
Cl(1)—Re(1)—O(3)	89.1(3)	Cl(3)—Re(2)—O(3)	87.7(3)
Cl(2)—Re(1)—S(1)	173.82(6)	Cl(4)—Re(2)—S(3)	174.16(7)
Cl(2)—Re(1)—S(2)	93.54(7)	Cl(4)—Re(2)—S(4)	90.12(8)
Cl(2)—Re(1)—O(1)	92.3(3)	Cl(4)—Re(2)—O(2)	106.1(4)
Cl(2)—Re(1)—O(3)	94.5(3)	Cl(4)—Re(2)—O(3)	95.3(3)
S(1)—Re(1)—S(2)	85.11(7)	S(3)—Re(2)—S(4)	86.58(8)
S(1)—Re(1)—O(1)	93.6(3)	S(3)—Re(2)—O(2)	78.9(4)
S(1)—Re(1)—O(3)	79.4(3)	S(3)—Re(2)—O(3)	79.7(3)
S(2)—Re(1)—O(1)	84.5(3)	S(4)—Re(2)—O(2)	92.6(3)
S(2)—Re(1)—O(3)	85.3(3)	S(4)—Re(2)—O(3)	85.7(3)
O(1)—Re(1)—O(3)	168.1(4)	O(2)—Re(2)—O(3)	158.6(5)

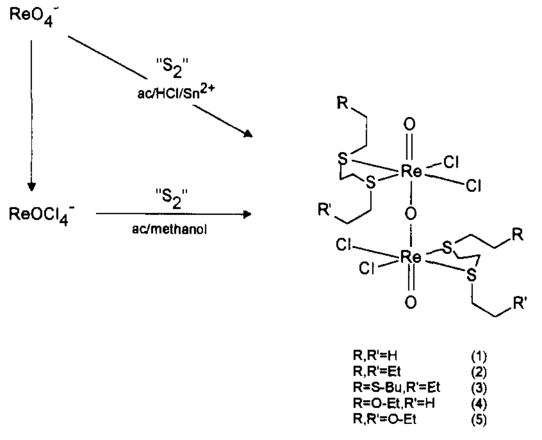

Fig. 1. Formation of the complexes **1–5** by reduction of perrhenate in the presence of the thioether or by ligand exchange reaction starting from [ReOCl$_4$]$^-$.

the other the potentially tridentate ligand 5,8,11-trithiapentadecane gives the bidentately coordinated complex, too.

The products are turquoise to green compounds which are readily soluble in CHCl$_3$, CH$_2$Cl$_2$ and acetonitrile, except for **1**, which is soluble only in dipolar aprotic solvents such as DMSO or DMF.

All the complexes show an intense and characteristic stretching vibration band between 650 cm^{-1} and 700 cm^{-1} indicating the Re—O—Re moiety, as reported previously for similar [M$_2$O$_3$]$^{4+}$ species (M = Tc, Re).[6,7]

Absorptions between 900 cm^{-1} and 1000 cm^{-1} which can be assigned to the Re = O^{3+} core were not observed.

Proton NMR studies indicate the diamagnetism of the complexes in agreement with the data reported previously for rhenium(V) d^2 species containing the ReO^{3+} and [Re$_2$O$_3$]$^{4+}$ cores in a distorted octahedral or in a square pyramidal coordination sphere.

Despite the complexity of the spectra due to the multiplicity of the methylene protons, three distinguishable groups of signals can be assigned: (i) triplets between 0.96 ppm and 1.2 ppm arising from the terminal —CH$_3$; (ii) broad multiplets between 1.5 ppm and 1.8 ppm describing the —CH$_2$CH$_2$— groups; and (iii) broad multiplets in the range from 3.1 to 4.1 ppm for —O—C$\underline{H}_2$, —S—C$\underline{H}_2$.

Molecular structure of μ-oxobis[(5,8-dithiadodecane)dichlorooxorhenium(V)] (**2**)

Single crystals suitable for X-ray analysis were obtained by slow evaporation of a chloroform/methanol solution.

A CELLGRAF[8] plot of **2** is shown in Fig. 2. Selected bond angles and distances are listed in Table 2.

Table 3. Melting points and analytical data of the complexes **1–5**

Complex	UV–vis [nm (lg ε)]	Melting point (°C)	Calc. (found)(%)			
			C	H	S	Cl
1	307(4.1) 620(2.6)	213–214	16.7 (16.7)	3.3 (3.3)	14.9 (14.7)	16.4 (16.4)
2	308(4.3) 618(2.7)	202–203	24.6 (24.6)	4.6 (4.5)	13.2 (13.1)	14.5 (14.6)
3	308(4.2) 619(2.7)	172–173	26.3 (26.3)	4.8 (4.7)	17.6 (17.5)	13.0 (13.2)
4	307(4.3) 616(2.7)	190–192	20.2 (20.2)	3.8 (3.7)	13.5 (13.3)	14.7 (14.9)
5	307(4.2) 617(2.6)	183–184	23.1 (23.2)	4.3 (4.2)	12.3 (12.4)	13.7 (13.8)

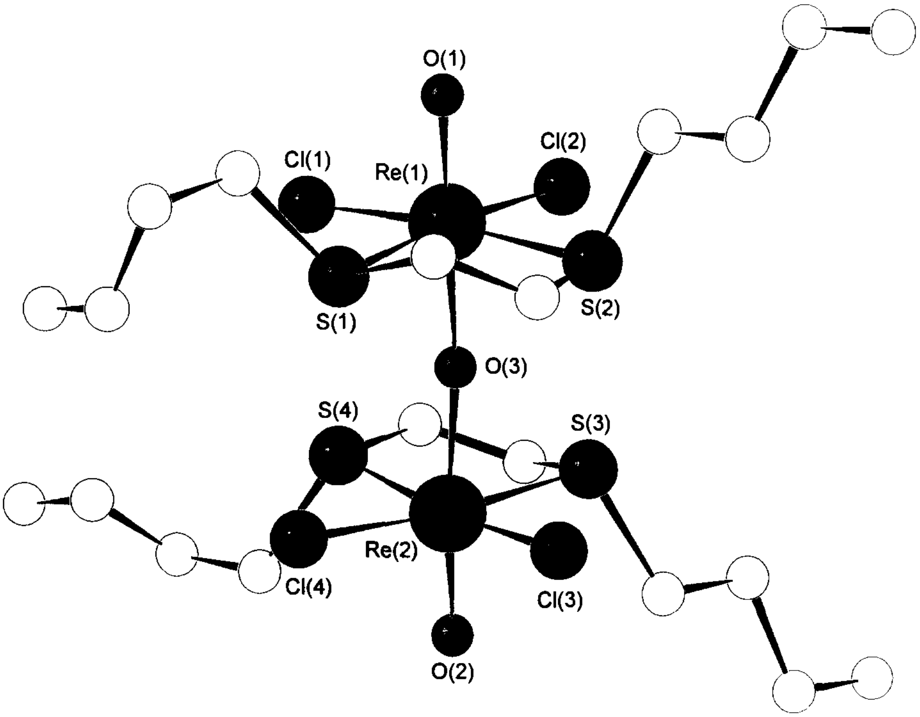

Fig. 2. CELLGRAF[8] drawing of [ReO(5,8-dithiadodecane)$_2$Cl$_2$]$_2$O (**2**).

Complex **2** consists of two independent [ReO(Bu—S—CH$_2$CH$_2$—S—Bu)Cl$_2$] units bridged by an oxygen atom. The characteristic feature is the presence of the O═Re—O—Re═O backbone which shows a considerable deviation from linearity. In this respect the structure of **2** is comparable to those found for the corresponding technetium complex [TcO("S$_2$")Cl$_2$]$_2$O ("S$_2$" = 5,8-dithiadodecane)[1] as well as for the rhenium complexes [ReO(pyr) $_2$]$_2$O (pyr = pridine)[9] and [ReO(1-Meim)$_2$Cl$_2$]$_2$ (1-Meim = 1-methylimidazole).[10]

As illustrated in Fig. 3 the rhenium atoms are centred in a octahedron with the equatorial plane formed by a S$_2$Cl$_2$ donor set, in which the metal atoms are 0.1141 Å {Re(1)} and 0.1213 Å {Re(2)} out-of-plane towards O(1) and O(2), respectively.

The octahedron is appreciably distorted, with the four equatorial ligands being displaced away from the Re═O bond. The effect is small for the atoms S(1), S(4), Cl(2) and Cl(3) which angles differ only few from ideal geometry (S(1)—Re(1)—O(1) = 93.6°, S(4)—Re(2)—O(2) = 92.6°, Cl(2)—Re(1)—O(1) =

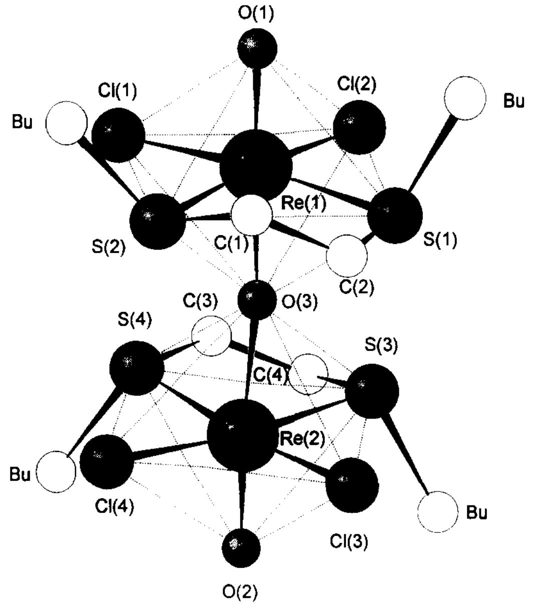

Fig. 3. Molecular geometry of [ReO(5,8-dithiadodecane)$_2$Cl$_2$]$_2$O (**2**) viewed perpendicular to the O(1), Re(1), O(3), Re(2), O(2) axis.

92.3°, Cl(3)—Re(2)—O(2) = 93.8°), but is more important for the atoms S(2), S(3), Cl(1) and Cl(4) (S(2)—Re(1)—O(1) = 84.5°, S(3)—Re(2)—O(2) = 78.9°, Cl(1)—Re(1)—O(1) = 100.7°, Cl(4)—Re(2)—O(2) = 106.1°).

The molecule adopts a staggered conformation in which the ReS_2Cl_2 planes are mutually rotated by 168° about the O=Re—O—Re=O axis.

The bond lengths of the Re=O cores of 1.705 and 1.735 Å are longer than commonly observed for sulphur- or nitrogen-coordinated square-pyramidal complexes (1.61–1.66 Å) but in the range generally found for O=$ReCl_2$—O— units (1.70–1.76 Å).

The bond distances and angles of the donor atoms fall in the range earlier observed for related compounds, so the bridging Re—O distances (Re(1)—O(3), 1.908 Å and Re(2)—O(3), 1.946 Å) are similar to those with the O=Re—O—Re=O backbone.[9,11]

The Re—Cl bonds (2.39–2.40 Å), *cis* to each other, fall in the region observed for the pyridine analogue (2.356–2.390 Å)[9] as well as the corresponding technetium/thioether complex (2.395–2.418 Å).[1]

Finally, the Re—S distances (2.410–2.439 Å) determined are in agreement with those found for other transition metal complexes with thioether coordination.[12]

This type of rhenium complex is worthy of special interest as manifold subsequent reactions can be anticipated. Diversity is given in ligand exchange reactions by various leaving groups in the coordination sphere, namely the only weakly bonded chelate and the two chloro ligands.

In this respect, studies on the reactivity and the electrochemical behaviour of the described complexes will follow.

Supplementary material—Additional X-ray crystal data can be obtained from Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-76344 Eggenstein–Leopoldshafen 2, Germany, quoting CSD-No. 401343, authors' names and the paper title.

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