Neutral Oxorhenium(V) Complexes with Tridentate Dithiolates and Monodentate Alkane- or Arene-thiolate Coligands†

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Oxorhenium(V) complexes [ReO(SXS)(SR)] (where HSXSH = 3-thia- or 3-oxa-pentane-1,5-dithiol and RSH = alkane- or arene-thiol) have been synthesized by a ligand exchange reaction of $[NEt_3(CH_2Ph)][ReOCl_4]$ with a mixture of HSXSH and RSH in methanol–acetonitrile. The compounds were purified by column chromatography or preparative TLC and characterized by elemental analysis, infrared and ^1H NMR spectroscopy. The structure of (4-methoxybenzenethiolato)(3-oxapentane-1,5-dithiolato)oxorhenium(V) has been determined by X-ray crystallography. The co-ordination is square-pyramidal with the Re atom displaced from the basal plane by 0.728 Å. Co-ordination of the ether group is indicated by the short Re–O(ether) bond distance of 2.103 Å.

Co-ordination compounds of rhenium play an important role in the search of nuclear medicine for new radiotracers. Particularly, ^{186}Re and ^{188}Re attract increasing interest, as these nuclides emit beta particles with therapeutically useful energies. In our efforts to design and evaluate new co-ordination compounds as a basis for potential rhenium tracers, we consider mixed-ligand complexes to be suitable for a rational tracer design. These compounds, which contain a chelating and a monodentate ligand, should be superior to compounds which contain one uniform ligand because a high degree of variability of the molecule can be achieved by modifying either the chelating or the monodentate ligand.

While for the congener technetium different types of mixed-ligand complexes exist, in which the monodentate ligands are a variety of thiolates,[1–5] rhenium complexes with monodentate thiolato ligands have been scarcely described so far.[6–10] The synthesis of six-co-ordinated rhenium(V) thiolato compounds containing terpyridine has recently been reported.[11] Moreover, selective formation of heterodimeric bis-bidentate oxorhenium(V) complexes was described.[12] The requirement for homologous substituted rhenium compounds prompted us to examine the usefulness of the '3 + 1' principle, earlier applied to the preparation of tridentate/monodentate mixed-ligand technetium(V) complexes,[3] for the synthesis of new lipophilic rhenium complexes. We report on the preparation and characterization of alkyl and aryl bearing oxorhenium(V) complexes of the general formula [ReO(SXS)(SR)] [HSXSH = $HSCH_2CH_2ECH_2CH_2SH$ (E = O or S); R = alkyl or aryl] and the X-ray crystal structure analysis of (4-methoxybenzenethiolato)-(3-oxapentane-1,5-dithiolato)oxorhenium(V).

Experimental

Materials and Methods.—Ammonium perrhenate was purchased from Aldrich. 3-Thiapentane-1,5-dithiol and 3-oxapentane-1,5-dithiol were obtained from Fluka.

Elemental analyses were performed on a LECO CHNS-932 elemental analyser. UV/VIS spectra were recorded on a Specord M40 from Carl Zeiss Jena. Infrared spectra (KBr pellets) were measured on a Specord M80. Proton NMR spectroscopy was carried out on a Bruker WH-90 device (solvent $CDCl_3$) and mass spectrometry was done using a Finnigan MAT 95 mass spectrometer. Thin layer chromatography of the complexes was done on silica gel (Silufol, Kavalier) with chloroform as the mobile phase. Column chromatography was done using Kieselgel 60 (0.04–0.063 mm) from Merck.

Preparations.—$[NEt_3(CH_2Ph)][ReOCl_4]$. To a suspension of ammonium perrhenate (1 g, 3.73 mmol) in ethanol (50 cm^3) was added benzyltriethylammonium chloride (934 mg, 4.1 mmol; 1.1 equivalents). Dry HCl was passed through the suspension which was converted 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 methanol (5 cm^3) and on slow addition of dry diethyl ether, the product was obtained as small light-orange needles (1.65 g, 82.5%), m.p. 95–98 °C ($MeOH–Et_2O$, decomp.) (Found: C, 29.1; H, 4.2; N, 2.4. $C_{13}H_{22}Cl_4NORe$ requires C, 29.1; H, 4.1; N, 2.6%). IR (KBr): 1008 cm^{-1} (ν_{ReO}).

*(4-Methoxybenzenethiolato)(3-oxapentane-*1,5*-dithiolato)oxorhenium*(V) **17**. A mixture of 3-oxapentane-1.5-dithiol (27.7 mg, 0.2 mmol) and 4-methoxybenzenethiol (22 mg, 0.2 mmol) in acetonitrile (1 cm^3) was added to a stirred solution of $[NEt_3(CH_2Ph)][ReOCl_4]$ (107 mg, 0.2 mmol) in methanol (1 cm^3) at 0 °C. A drop of triethylamine was then added and the reaction mixture changed from green to deep brown immediately, and a brown precipitate was deposited. After stirring for another hour the solid material was separated. It was dissolved in hot chloroform and purified by column chromatography using chloroform as eluent. Addition of a few cm^3 of ethanol to the eluate and evaporation of most of the solvent gave the pure product as small dark-brown needles. Yield 63% (60 mg). A second crop of **17** can be obtained by evaporating the reaction solvent.

Complexes **10**, **11**, **15**, **16**, **18** and **19** are accessible in similar yields by the same procedure. The working-up procedure was

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† *Supplementary data available:* Further details of the structure determination (complete bond lengths and angles, H-atom coordinates, structure factors, thermal parameters) have been deposited at The Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-76344 Eggenstein-Leopoldshafen 2, Germany. Any request for this material should quote a full literature citation and the reference number CSD 401649.

modified for the alkyl- and (aryl)alkyl-substituted complexes **1**–**9** and **12**–**14** because these compounds did not precipitate under the above conditions. The raw complexes can be isolated from the reaction mixture by evaporation to dryness, dissolution in chloroform, removal of insoluble by-products and column chromatography. Pure compounds were obtained in 20–35% yields although sometimes yields of up to 65% were obtained for aryl-substituted complexes. However, especially when 3-oxapentane-1,5-dithiol was employed as the tridentate ligand or when long-chain thiols were used as coligands, formation of oils was found to occur.

Structure Determination.—Crystal data. $C_{11}H_{15}O_3ReS_3$; $M = 477.63$, monoclinic, $a = 7.514(4)$, $b = 14.767(4)$, $c = 13.962(2)$ Å, $\beta = 103.70(2)°$, $U = 1476$ Å^3 (by least-squares refinement of Bragg angles for 25 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P2_1/c$ (no. 14), $Z = 4$, $D_c = 2.15$ g cm^{-3}, $F(000) = 912$, $T = 296$ K. Red-brown, air-stable crystals. Crystal dimensions $0.07 \times 0.09 \times 0.36$ mm, μ(Mo-Kα) = 87.49 cm^{-1}.

Data collection and processing. CAD4 diffractometer, ω–2θ mode with ω-scan width = $0.85 + 0.35 \tan\theta$, ω scan speed 1.4–4.8° min^{-1}, graphite-monochromated Mo-Kα radiation; 2928 unique reflections measured ($1.5 < \omega \leqslant 25°$, $\pm h, k, l$), giving 2402 reflections with $I > 2\sigma(I)$, empirical correction (min. and max. transmission factors 0.845, 0.999).

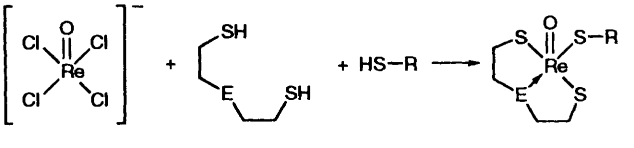
Structure analysis and refinement. Direct methods (Re and S atoms) followed by normal heavy-atom procedures. Full-matrix least-squares refinement on F with all non-hydrogen atoms anisotropic and hydrogens in calculated positions with fixed isotropic thermal parameters. The weighting scheme $w = 1.0$ for $F <$ threshold $w = [\text{threshold}/F]^2$ for $F >$ threshold; threshold = 80% of the largest F. Final R and R' values are 0.028 and 0.030, respectively. For programs used and sources of scattering factor data see ref.13.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles

Results and Discussion

When a 1 : 1 molar ratio mixture of HSXSH and the alkanethiol or substituted benzenethiol in acetonitrile is added to a stirred solution of $[NEt_3(CH_2Ph)][ReOCl_4]$ in methanol at 0 °C, neutral alkyl- and aryl-substituted oxorhenium(V) complexes [ReO(SXS)(SR)] are formed according to Scheme 1. The reaction can also be carried out in acetone, chloroform, ethanol or any mixture of them without interferences or diminishing of yields. The compounds are also accessible starting from $[ReOCl_3(PPh_3)_2]$ with equimolar amounts of the ligands in chloroform solution. The reaction mixture must be briefly heated to complete the reaction in an appropriate time. However, the yields obtained by this reaction are lower than reported for the ligand-exchange reaction with $[ReOCl_4]^-$.

Complexes with aromatic thiols (**10**, **11**, **15**–**19**) precipitate from the mixture and were purified by column chromatography with chloroform. The compounds crystallize after addition of ethanol to the eluate and reduction of volume of the solvents. Aliphatic substituted compounds do not precipitate from the reaction mixture and were purified either by column chromatography or by preparative thin-layer chromatography.



Scheme 1 The '3 + 1' method for the synthesis of mixed-ligand complexes

Compounds derived from long-chain thiols tend to form oils and are often difficult to crystallize. The yields of pure compounds are in the region from 20% up to 65%.

The air-stable compounds are soluble in acetone, acetonitrile, chloroform and methylene chloride, insoluble in water, and all, except **7**, almost insoluble in ethanol and diethyl ether. Furthermore, the complexes can be heated in and crystallized from these solvents without decomposition. However, the compounds decompose when exposed to sodium hydroxide or ammonia solutions giving products which are insoluble in common solvents. The elemental analysis of the compounds (C, H, S) corresponds to the general formula [ReO(SXS)(SR)], which is confirmed by ^{1}H NMR and IR spectroscopy. The elemental analysis of compound **1**, however, shows a low sulfur value which persists despite various purification attempts.

Elemental analyses and spectroscopic data of all compounds are summarized in Tables 1 and 2. (4-Methoxybenzenethiolato)(3-oxapentane-1,5-dithiolato)oxorhenium(V) **17** was chosen as a typical representative of the class of complexes covered herein and is discussed below.

Complex **17** shows a strong Re=O stretching vibration at 968 cm^{-1}. In the IR spectra of all the other rhenium(V) complexes examined, the Re=O bands were found in the region 950–980 cm^{-1}. The wavenumbers of the respective bands of complexes **1**–**11** (E = S) are generally somewhat lower than those of complexes **12**–**19** (E = O). In comparison to these values, the Re=O band in $[ReOCl_4]^-$ is found at 1008 cm^{-1}.

The ^{1}H NMR spectrum of **17** exhibits an assembly of three broad signals for the methylene protons of $-SCH_2CH_2OCH_2CH_2S-$ at δ 4.68, 3.73 and 3.2–3.6. The signals of the monodentate ligand are seen at δ 7.51 and 6.96 for the aromatic protons and δ 3.84 for OCH_3. The NMR data of all the complexes **1**–**19** are listed in Table 2. They show that the patterns of methylene protons of the complexes where E = S are clearly distinguished from those where E = O. Within each series, the patterns of the protons of the tridentate ligand do not show major differences. In this respect the rhenium compounds are similar to the analogous technetium complexes.[3]

The UV spectra (recorded in acetonitrile) of the complexes with E = S are characterized by an intense band at 384–400 nm (log ε = 3.3–3.7), those with E = O have a typical band at *ca.* 344–362 nm (3.5–3.8). Within each series, the aryl substituted complexes show absorptions at higher wavelengths. Further bands and shoulders are seen at 222–235 nm (3.8–4.3), 252–255 nm (3.7–4.2) and 505–530 nm (1.9–2.2),

Additionally, **17** was characterized by mass spectrometry and by its crystal structure.

In the 70 eV (*ca* 1.12×10^{-17} J) electron impact (EI) mass spectrum of **17**, a line cluster at *m*/*z ca.* 478 shows the typical intensity distribution expected for $C_{11}H_{15}O_3ReS_3$ ions so confirming the proposed composition. Besides the line cluster of the molecular ion, the EI spectrum of **17** shows some typical rhenium-containing fragment ions at *m*/*z* 450 ($M - C_2H_4$), 422 ($M - 2\,C_2H_4$) and 390 ($M - 2\,C_2H_4$, $-$S) as well as the base peak at *m*/*z* 139 due to the 4-methoxybenzenethiolate ion. Line clusters at *m*/*z ca.* 484, 500, 516, 532 and 548 with typical isotopic patterns result from $Re_2O_xS_y$ species showing the partial decomposition of **17** in the ion source during heating. Complex **17** is more clearly characterized by its negative chemical ionization MS. In the case of soft ionization with isobutane only the loss of the 4-methoxybenzenethiol ligand is observed to a small extent besides the strong base peak of the molecular ion at *m*/*z ca.* 478.

The co-ordination in **17** (Fig. 1) is distorted square-pyramidal with the metal atom 0.728 Å above the plane formed by the four donor atoms. Whereas a square-pyramidal arrangement is also found in many oxorhenium(V) complexes containing two bidentate ligands or a tetradentate ligand, **17** shows two novel features. First the basal plane is built up by two different organic ligands, a tridentate and a monodentate one. The second interesting aspect of this complex is that an ether oxygen

Table 1 List of complexes [ReO(SXS)(SR)] [X = $CH_2CH_2ECH_2CH_2$ (E = O or S)] and analytical data

Compound	E	R	Formula	M.p.[a]/°C ($CHCl_3$–EtOH)	Elemental analysis[b] (%)		
					C	H	S
1	S	Me	$C_5H_{11}OReS_4$	166–169	15.0 (15.0)	2.7 (2.8)	30.3 (31.9)
2	S	Et	$C_6H_{13}OReS_4$	163–165	17.2 (17.3)	3.1 (3.1)	30.8 (30.9)
3	S	Pr^n	$C_7H_{15}OReS_4$	143–145	19.5 (19.6)	3.4 (3.5)	30.1 (29.9)
4	S	Pr^i	$C_7H_{15}OReS_4$	175–178	19.6 (19.6)	3.4 (3.5)	29.7 (29.9)
5	S	Bu^n	$C_8H_{17}OReS_4$	107–108	21.5 (21.6)	3.8 (3.9)	28.9 (28.9)
6	S	Bu^i	$C_8H_{17}OReS_4$	138–140	21.6 (21.7)	3.8 (3.9)	28.8 (28.9)
7	S	$C_{12}H_{25}$	$C_{16}H_{33}OReS_4$	69–70	34.3 (34.6)	5.9 (6.0)	22.8 (23.1)
8	S	$PhCH_2$	$C_{11}H_{15}OReS_4$	177–179	27.6 (27.7)	3.1 (3.2)	27.1 (26.9)
9	S	$PhCH_2CH_2$	$C_{12}H_{17}OReS_4$	162–164	29.0 (29.3)	3.3 (3.5)	26.0 (26.1)
10	S	Ph	$C_{10}H_{13}OReS_4$	211–213	26.0 (25.9)	3.0 (2.8)	27.8 (27.7)
11	S	C_6H_4OMe-*p*	$C_{11}H_{15}O_2ReS_4$	217–219	26.5 (26.8)	3.0 (3.1)	26.1 (26.0)
12	O	Me	$C_5H_{11}O_2ReS_3$	135–137	15.7 (15.6)	2.7 (2.9)	25.1 (25.0)
13	O	Et	$C_6H_{13}O_2ReS_3$	99–100	18.3 (18.0)	3.3 (3.3)	24.1 (24.1)
14	O	Pr^i	$C_7H_{15}O_2ReS_3$	158–160	20.3 (20.3)	3.6 (3.7)	23.2 (23.3)
15	O	Ph	$C_{10}H_{13}O_2ReS_3$	193–195	26.4 (26.8)	3.0 (2.9)	21.3 (21.5)
16	O	C_6H_4Me-*p*	$C_{11}H_{15}O_2ReS_3$	206–208	28.6 (28.6)	3.3 (3.3)	20.6 (20.8)
17	O	C_6H_4OMe-*p*	$C_{11}H_{15}O_3ReS_3$	197–199	27.4 (27.7)	3.2 (3.2)	20.4 (20.1)
18[c]	O	C_6H_4Cl-*p*	$C_{10}H_{12}ClO_2ReS_3$	202–204	24.7 (24.9)	2.5 (2.5)	20.1 (20.0)
19[d]	O	C_6H_4Br-*p*	$C_{10}H_{12}BrO_2ReS_3$	196–198	22.5 (22.8)	2.2 (2.3)	18.0 (18.3)

[a] With decomposition. [b] Required values given in parentheses. [c] Cl: 7.6 (7.4)%. [d] Br: 15.4 (15.2)%.

Table 2 Spectroscopic data for compounds **1**–**19**

Compound	ν(Re=O)[a]/cm^{-1}	δ_H $SCH_2CH_2ECH_2CH_2S$	SR
1	960	1.96 (2 H), 3.12 (2 H), 3.92 (2 H), 4.30 (2 H)	3.42 (s, 3 H, SMe)
2	962	1.96 (2 H), 3.12 (2 H), 3.90 (2 H),[b] 4.29 (2 H)	1.55 (t, 3 H, Me), 3.88 (2 H, CH_2)[b]
3	960	1.93 (2 H), 3.09 (2 H), 3.83 (2 H),[b] 4.27 (2 H)	1.09 (t, 3 H, Me), *ca.* 1.9 (2 H, CH_3CH_2), 3.82 (t, 2 H, SCH_2)[b]
4	968	1.92 (2 H), 3.09 (2 H), 3.90 (2 H), 4.28 (2 H)[b]	4.35 (spt, 1 H, $CHMe_2$), 1.58 (d, 6 H, Me)
5	960	1.94 (2 H),[b] 3.11 (2 H), 3.91 (2 H),[b] 4.28 (2 H)	0.96 (t, 3 H, Me), 1.55 (sxt, 2 H, CH_3CH_2), 1.88 (qnt, 2 H, $CH_3CH_2CH_2$),[b] 3.85 (t, 2 H, SCH_2)[b]
6	960	1.93 (2 H),[b] 3.09 (2 H), 3.89 (2 H), 4.27 (2 H)	1.09 (d, 6 H, Me), 2.21 (nonet, CH_2CHMe_2),[b] 3.73 (d, 2 H, CH_2)
7	960	1.91 (2 H), 3.11 (2 H), 3.91 (4 H),[b] 4.28 (2H)	0.88 (t, 3 H, Me), 1.26 (16 H), 1.55 (m, 2 H, CH_2CH_3), 1.88 (qnt, 2 H, SCH_2CH_2), 3.89 (t, 2 H, SCH_2)[b]
8	960	1.95 (2 H), 3.12 (2 H), 3.91 (2 H), 4.29 (2 H)	5.02 (s, 2 H, SCH_2Ph), 7.05–7.54 (m, 5 H, Ph)
9	960	1.93 (2 H), 3.10 (2 H),[b] 3.87 (2 H),[b] 4.33 (2 H)[b]	*ca.* 3.1 (m, $PhCH_2$), *ca.* 4.0 (m, SCH_2),[b] 7.29 (Ph)
10	960	2.02 (2 H), 2.98 (2 H), 3.87 (2 H), 4.07 (2 H)	7.02–7.64 (5 H, Ph)
11	956	1.99 (2 H), 3.10 (2 H), 3.94 (2 H), 4.19 (2 H)	3.85 (s, 3 H, OCH_3), 6.94 (2 H, *o*-H to OMe), 7.60 (2 H, *m*-H to OMe)
12	969	3.10–4.04 (6 H), 4.65 (2 H)	3.41 (s, 3 H, SCH_3)
13	960	3.08–4.00 (6 H),[b] 4.64 (2 H)	1.48 (t, 3 H, Me), 3.45 (2 H, SCH_2)[b]
14	967	3.45 (m, 6 H), 4.62 (2 H, br)	1.53 (6 H, Me, br),[c] 4.32 (spt, $CHMe_2$)
15	966	3.34 (4 H, br), 3.70 (2 H), 4.68 (2 H)	7.08–7.67 (5 H; arom.)
16	967	3.24 (4 H, br), 3.67 (2 H), 4.63 (2 H)	2.32 (3 H, CH_3), 7.11 (2 H, *o*-H to OMe), 7.36 (2 H, *m*-H to OMe)
17	968	3.2–3.6 (4 H, br), 3.73 (2 H), 4.68 (2 H)	3.84 (s, 3 H, OCH_3), 6.96 (2 H, C_6H_4), 7.51 (2 H, C_6H_4)
18	976	3.35 (4 H, br), 3.73 (2 H), 4.70 (2 H)	7.3–7.5 (4 H, C_6H_4, AA′BB′)
19	968	3.35 (4 H, br), 3.76 (2 H), 4.70 (2 H)	7.49 (s, 4 H, C_6H_4, AA′BB′)

[a] In KBr pellet. [b] Overlapping signals. [c] The transformation of the two singlets for the methyl protons (as seen in **4** and in free propan-2-thiol) into one broad signal seems to be due to rotational barriers. A 200 MHz proton NMR spectrum resolves this signal into two broad signals at δ 1.43, 1.67.

donor atom is involved in the co-ordination sphere of rhenium, the Re–O bond length being 2.103 Å. The strength of the Re–O bond should be compared with those of the two neighbouring very stable Re–S bonds. The bond lengths of the multiple rhenium–oxygen bond and the rhenium–sulfur bonds fall in the normal range reported for various oxorhenium complexes.

This work demonstrates the selective formation of mixed-ligand complexes with all tridentate/monodentate ligand combinations used. Once the complexes had formed, addition of different thiols or other ligands did not lead to ligand-exchange reactions. Formation of binuclear complexes $[(ReO)_2(SXS)_3]$ which can be expected when one SXS^{2-} acts as a bridging ligand between two [ReO(SXS)] (as found for Tc^V) was not observed.

Therefore stable neutral rhenium complexes are available in which one site can easily be modified by a large variety of substituents. Additional modifications can be made by choosing appropriate X groups in the tridentate ligand. Unlike complexes formed with bidentate and tetradentate ligands, in which introduction of substituents onto the carbon atom backbone of the ligands delivers stereogenic centres, there are no complications concerning the stereochemistry in the described complexes. We think that this class of '3 + 1'-

Table 3 Atomic coordinates for complex **17** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Re	0.218 28(4)	0.027 05(2)	0.215 91(2)
S(1)	0.203 1(3)	0.179 6(1)	0.197 5(2)
S(2)	0.355 9(3)	0.013 9(1)	0.085 2(1)
S(4)	−0.075 5(3)	0.042 1(2)	0.234 6(2)
O(1)	0.365 2(8)	0.008 5(4)	0.325 3(4)
O(2)	0.791 6(7)	0.349 2(3)	0.039 5(4)
O(3)	0.111 3(6)	−0.099 3(3)	0.160 1(3)
C(1)	0.347(1)	−0.109 9(5)	0.070 0(6)
C(2)	0.166(1)	−0.142 6(5)	0.075 0(6)
C(3)	−0.075(1)	−0.126 1(5)	0.160 8(6)
C(4)	−0.132(1)	−0.077 0(6)	0.244 2(6)
C(5)	0.378 3(9)	0.226 8(4)	0.144 2(5)
C(6)	0.332(1)	0.285 9(5)	0.062 9(5)
C(7)	0.464(1)	0.328 4(4)	0.025 5(5)
C(8)	0.646(1)	0.311 6(4)	0.069 1(5)
C(9)	0.692 7(9)	0.252 0(5)	0.148 6(6)
C(10)	0.560 0(9)	0.211 0(4)	0.185 0(5)
C(11)	0.757(1)	0.420 5(6)	−0.030 3(6)

Table 4 Selected bond lengths (Å) and angles (°) for complex **17** with e.s.d.s. in parentheses

Re–S(1)	2.267(2)	S(2)–C(1)	1.840(8)
Re–S(2)	2.277(2)	S(4)–C(4)	1.821(9)
Re–S(4)	2.293(2)	O(3)–C(2)	1.47(1)
Re–O(1)	1.659(5)	O(3)–C(3)	1.461(9)
Re–O(3)	2.103(4)	C(1)–C(2)	1.46(1)
S(1)–C(5)	1.790(7)	C(3)–C(4)	1.50(1)
S(1)–Re–S(2)	91.00(7)	Re–S(2)–C(1)	99.3(3)
S(1)–Re–S(4)	83.78(8)	Re–S(4)–C(4)	99.3(3)
S(1)–Re–O(1)	105.6(2)	Re–O(3)–C(2)	121.4(4)
S(1)–Re–O(3)	146.8(1)	Re–O(3)–C(3)	121.5(4)
S(2)–Re–S(4)	136.42(7)	C(2)–O(3)–C(3)	109.6(5)
S(2)–Re–O(1)	111.5(2)	S(2)–C(1)–C(2)	109.5(6)
S(2)–Re–O(3)	81.0(1)	O(3)–C(2)–C(1)	109.3(6)
S(4)–Re–O(1)	111.6(2)	O(3)–C(3)–C(4)	108.7(6)
S(4)–Re–O(3)	80.3(1)	S(4)–C(4)–C(3)	107.5(6)
O(1)–Re–O(3)	107.3(2)	S(1)–C(5)–C(6)	120.1(5)
Re–S(1)–C(5)	114.2(2)	S(1)–C(5)–C(10)	121.8(5)

compounds has considerable potential in the design of new functionalized technetium and rhenium complexes. Currently we are engaged in experiments to introduce reactive substituents in the side chain of the monodentate ligand to make the complexes more reactive and to modify lipophilicity.

Conclusion

Starting from $[ReOCl_4]^-$, a monothiol and 3-thia- or 3-oxapentane-1,5-dithiol, nineteen new lipophilic oxorhenium(v) complexes have been synthesized and characterized by IR and ^1H NMR spectroscopy. (4-Methoxybenzenethiolato)(3-oxapentane-1,5-dithiolato)oxorhenium(v) **17** as a typical example of the class of compounds described herein was additionally characterized by mass spectrometry and X-ray structure analysis. It shows distorted square-pyramidal co-ordination of the donor ligands with the ether oxygen co-ordinated to the Re atom with a bond distance of 2.103 Å.

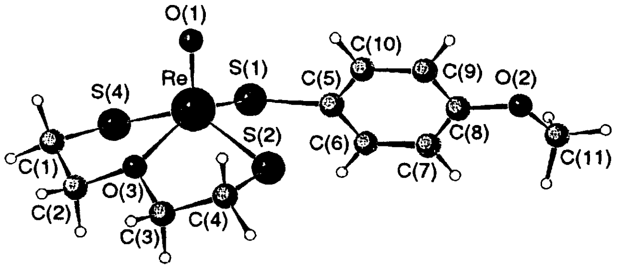


Fig. 1 Molecular structure of complex **17**, with a partial atom labelling scheme

The Re=O distance is 1.659 Å; the Re atom is displaced from the basal plane by 0.728 Å. Rhenium complexes with tridentate/monodentate ligand co-ordination allow a novel access to rhenium tracers for nuclear medicine since their lipophilicity can be easily tuned by modifying one of the ligands.

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