metal-organic compounds

(4-Methoxybenzenethiolato-κS)oxido-[2,2′-(propylimino)bis(ethanethiolato)-κ³S,N,S′]rhenium(V)

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The central Re atom of the mononuclear title complex, $[Re(C_8H_{18}NS_2)(C_6H_4OS)O]$, is five-coordinate $(ReNOS_3)$ with a square-pyramidal geometry comprising a tridentate 2,2′-(propylimino)diethanethiolate ligand, a 4-methoxybenzenethiolate ligand and a doubly-bonded O atom.

Related literature

Similar complexes are currently under study as model compounds with regard to the development of novel technetium-based radiopharmaceuticals for the non-invasive diagnosis of myocardial metabolism, see: Chelminiak *et al.* (2005); Femia *et al.* (2000); Friebe *et al.* (2000); Heimbold *et al.* (2002); Jung *et al.* (2002); Maresca *et al.* (2002); Marsh (2005). For related literature, see: Allen (2002); Corbin *et al.* (1984); Noll *et al.* (2002).
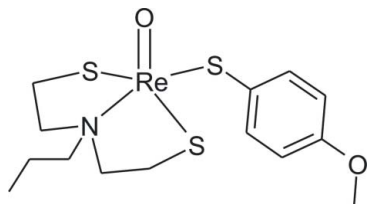
Experimental

Crystal data

C₁₄H₂₂NO₂ReS₃

$C_{14}H_{22}NO_2ReS_3$
M_r = 518.71
Monoclinic, $P2_1/c$
a = 12.160 (3) Å
b = 16.809 (4) Å
c = 9.441 (2) Å
β = 111.459 (4)°

V = 1796.0 (7) Å³
Z = 4
Mo $K\alpha$ radiation
μ = 7.12 mm⁻¹
T = 295 (2) K
0.45 × 0.4 × 0.2 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.058, T_{max} = 0.247

10348 measured reflections
4013 independent reflections
2835 reflections with $I > 2\sigma(I)$
R_{int} = 0.060

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.078
S = 0.89
4013 reflections

190 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.68 e Å⁻³
$\Delta\rho_{min}$ = −1.24 e Å⁻³

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12B···O1	0.97	2.59	2.971 (7)	104

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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supplementary materials

(4-Methoxybenzenethiolato-*κS*)oxido[2,2'-(propylimino)bis(ethanethiolato)-*κ*³*S*,*N*,*S*'']rhenium(V)

W. Kraus, F. Emmerling, B. Noll, S. Noll and H.-J. Pietzsch

Comment

Recently a new method has been described that allows to use metal complexes as prosthetic groups in fluorine-18 labelling of biologically relevant molecules (Noll *et al.*, 2002). The principle is based on labelling a tridentate dithiole ligand with ^{18}F and combining it with a monodentate thiole ligand to form mixed-ligand rhenium complexes. To better understand the reaction route a non-radioactive fluorine model compound was prepared and all by-products obtained were characterized by X-ray structure analysis, among them the title compound. Similar complexes are currently under study as model compounds with regard to the development of novel technetium-based radiopharmaceuticals for the noninvasive diagnosis of myocardial metabolism (Chelminiak *et al.*, 2005, Femia *et al.*, 2000, Friebe *et al.*, 2000, Heimbold *et al.*, 2002, Jung *et al.*, 2002, Maresca *et al.*, 2002, Marsh, 2005).

The molecular structure of the title complex reveals a neutral square pyramidal mononuclear complex, depicted in Fig. 1. The Re atom is coordinated by two sulfur atoms and a nitrogen atom from the tridentate ligand; another sulfur atom from the 4-methoxybenzenethiol ligand and an additional oxygen atom complete the square pyramidal coordination sphere with an axial Re—O distance of 1.679 (4) Å, a Re—N distance of 2.189 (5) Å and with Re—S bond lengths ranging from 2.2762 (16) to 2.3030 (16) Å. The Re—S3—C5 angle between the methoxyphenyl moiety and the central Re atom amounts to 110.64 (18)°, the torsion angle S2—Re—S3—C5 to −35.52 (1)°. The values mentioned above are in good agreement with those reported in the CCSD (Version 5.27; Allen, 2002); ($d_{Re—O}$ = 1.663–1.720 Å, av: 1.693 Å; $d_{Re—N}$ = 2.149–2.245 Å, av: 2.213 Å; $d_{Re—S}$ = 2.221–2.320 Å, av. 2.287 Å). The averages are based on 45 structures. A weak intramolecular hydrogen bond can be found in the crystal structure, namely C12—H12B ⋯ O1 with H ⋯ A=2.59, D ⋯ A=2.971 (6) Å and an inclined angle of 103°. It should be noticed, that this hydrogen bond is more likely a result of the compound geometry than of any attractive interaction. The analysis of the crystal packing reveals that no classic hydrogen bonds and π-π interactions are present. The head to tail arrangement of the molecules within the layers leads to a zigzag formation of the Re atoms along the *c* axis, with a Re—Re distance of 6.7410 (2) Å (Fig. 2.).

Experimental

The first intermediate bis(2-benzylthioethyl)amine was prepared by the reaction of benzyl mercaptane and bis(2-chloroethyl)amine hydrochloride (Fluka) as described in (Corbin *et al.*, 1984). Then the hydroxypropyl group was introduced by reaction of bromopropanol with the bis(2-benzylthioethyl)amine. For fluorination of this compound it was necessary to insert a tosyl group at the hydroxypropyl group as leaving group. In the next step the flourine was introduced by nucleophilic substitution using the KF crown ether kryptofix 2.2.2 complex in acetonitrile at 140°C. Subsequent both benzyl protecting groups were split off by reductive cleavage in liquid ammonia and metallic sodium to get the fluorine substituted tridentate NS2 ligand. This reaction is accompanied by a competitive reaction forming the *N*,*N*-bis(mercaptoethyl)-*N*-(propyl)amine by cleavage the flourine. Without further purification the reaction mixture was combined with the monodentate *p*-methoxy benzene thiol ligand as model compound and Re at the oxidation state +5 to give "3 + 1" complexes. The two Re complexes were separated by column chromatography on silica gel and methylene chloride as eluent. The fractions were collected and

supplementary materials

evaporated to dryness. The crystals of the metal complex were grown from ethanol. Here we describe the metal complex of the by-product as shown in Fig. 3.

Refinement

All H atoms were included using a riding model, with C–H: 0.93–0.97 Å, $U(H)_{iso}=1.2–1.5\times U(host)_{equiv}$. The H atoms of the methyl group were treated as being static.
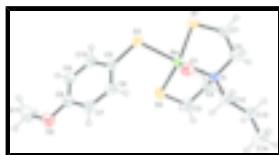
Figures

Fig. 1. : Molecular structure of the title compound, shown with 30% probability displacement ellipsoids. The intramolecular hydrogen bond is indicated *via* a dotted line.
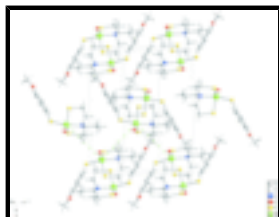
Fig. 2. : The crystal packing of the title compound, showing the Re—Re distance of 6.7410 (2) Å (dotted line).

Fig. 3. : Synthesis of the tridentate ligand and the by-products occurring after reductive cleavage of the protecting groups

(4-Methoxybenzenethiolato-κS)oxido[2,2'-(propylimino)bis(ethanethiolato)- κ³S,N,S']rhenium(V)

Crystal data

$C_{14}H_{22}NO_2ReS_3$	$F_{000} = 1008$
$M_r = 518.71$	$D_x = 1.918$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 1013 reflections
$a = 12.160$ (3) Å	$\theta = 2.7–27.9°$
$b = 16.809$ (4) Å	$\mu = 7.12$ mm^{-1}
$c = 9.441$ (2) Å	$T = 295$ (2) K
$\beta = 111.459$ (4)°	Needle, red
$V = 1796.0$ (7) Å^3	$0.45 \times 0.4 \times 0.2$ mm
$Z = 4$	

Data collection

Bruker SMART CCD diffractometer	4013 independent reflections
Radiation source: fine-focus sealed tube	2835 reflections with $I > 2\sigma(I)$

Monochromator: graphite	$R_{int} = 0.060$	
$T = 295(2)$ K	$\theta_{max} = 27.5°$	
ω–scan	$\theta_{min} = 2.2°$	
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -12 \rightarrow 15$	
$T_{min} = 0.058$, $T_{max} = 0.247$	$k = -18 \rightarrow 21$	
10348 measured reflections	$l = -12 \rightarrow 11$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.035$	H-atom parameters constrained
$wR(F^2) = 0.078$	$w = 1/[\sigma^2(F_o^2) + (0.0372P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.89$	$(\Delta/\sigma)_{max} = 0.001$
4013 reflections	$\Delta\rho_{max} = 1.68$ e Å^{-3}
190 parameters	$\Delta\rho_{min} = -1.24$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Re	0.700310 (19)	0.893135 (12)	0.01570 (2)	0.04417 (9)
S2	0.72046 (17)	1.02603 (9)	0.06904 (18)	0.0645 (5)
S1	0.52443 (14)	0.82875 (9)	−0.04378 (17)	0.0609 (4)
S3	0.63447 (14)	0.92485 (10)	−0.23912 (16)	0.0575 (4)
N	0.7014 (4)	0.8856 (2)	0.2477 (5)	0.0473 (11)
O1	0.8211 (3)	0.8372 (2)	0.0448 (4)	0.0608 (11)
O2	0.8870 (4)	1.2026 (3)	−0.3639 (5)	0.0802 (14)
C1	0.5151 (6)	0.8080 (4)	0.1407 (6)	0.0689 (18)
H1B	0.4615	0.8455	0.1597	0.083*
H1C	0.4837	0.7549	0.1402	0.083*
C2	0.6344 (6)	0.8141 (4)	0.2648 (7)	0.0703 (19)

H2A	0.6249	0.8166	0.3623	0.084*
H2B	0.6797	0.7667	0.2641	0.084*
C3	0.7113 (6)	1.0310 (3)	0.2570 (6)	0.0638 (17)
H3A	0.7902	1.0329	0.3343	0.077*
H3B	0.6696	1.0789	0.2655	0.077*
C4	0.6471 (5)	0.9593 (3)	0.2808 (6)	0.0544 (15)
H4A	0.6508	0.9581	0.3852	0.065*
H4B	0.5647	0.9621	0.2143	0.065*
C5	0.7100 (5)	1.0101 (3)	−0.2697 (6)	0.0483 (14)
C6	0.8320 (5)	1.0194 (4)	−0.2006 (6)	0.0553 (15)
H6A	0.8766	0.9817	−0.1313	0.066*
C7	0.8863 (6)	1.0841 (4)	−0.2349 (7)	0.0605 (16)
H7A	0.9677	1.0898	−0.1882	0.073*
C8	0.8217 (6)	1.1413 (4)	−0.3381 (7)	0.0573 (15)
C9	0.7015 (6)	1.1325 (4)	−0.4051 (7)	0.0582 (16)
H9A	0.6569	1.1704	−0.4739	0.070*
C10	0.6463 (5)	1.0677 (4)	−0.3710 (6)	0.0570 (15)
H10A	0.5647	1.0627	−0.4169	0.068*
C11	0.8255 (7)	1.2612 (4)	−0.4715 (9)	0.101 (3)
H11A	0.8803	1.3004	−0.4794	0.151*
H11B	0.7677	1.2862	−0.4391	0.151*
H11C	0.7867	1.2366	−0.5689	0.151*
C12	0.8277 (5)	0.8757 (3)	0.3550 (6)	0.0576 (16)
H12A	0.8746	0.9178	0.3351	0.069*
H12B	0.8572	0.8256	0.3320	0.069*
C13	0.8477 (7)	0.8768 (4)	0.5254 (7)	0.074 (2)
H13A	0.8189	0.9267	0.5500	0.088*
H13B	0.8027	0.8341	0.5473	0.088*
C14	0.9746 (8)	0.8674 (6)	0.6222 (8)	0.124 (3)
H14A	0.9835	0.8685	0.7275	0.186*
H14B	1.0192	0.9100	0.6019	0.186*
H14C	1.0029	0.8175	0.5996	0.186*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Re	0.04516 (15)	0.04144 (14)	0.04578 (15)	0.00048 (10)	0.01648 (10)	−0.00574 (10)
S2	0.1001 (14)	0.0421 (8)	0.0571 (9)	−0.0062 (8)	0.0356 (9)	−0.0031 (7)
S1	0.0518 (9)	0.0694 (10)	0.0571 (9)	−0.0097 (8)	0.0146 (7)	−0.0114 (8)
S3	0.0595 (10)	0.0647 (9)	0.0461 (8)	−0.0043 (8)	0.0166 (7)	−0.0062 (7)
N	0.045 (3)	0.040 (3)	0.053 (3)	0.000 (2)	0.014 (2)	−0.003 (2)
O1	0.062 (3)	0.056 (3)	0.064 (2)	0.004 (2)	0.023 (2)	−0.008 (2)
O2	0.087 (4)	0.069 (3)	0.079 (3)	−0.009 (3)	0.024 (3)	0.015 (2)
C1	0.070 (5)	0.076 (4)	0.062 (4)	−0.028 (4)	0.028 (3)	−0.008 (3)
C2	0.079 (5)	0.065 (4)	0.062 (4)	−0.021 (4)	0.019 (3)	0.002 (3)
C3	0.088 (5)	0.051 (4)	0.054 (4)	0.010 (3)	0.027 (3)	−0.007 (3)
C4	0.056 (4)	0.059 (4)	0.049 (3)	0.005 (3)	0.021 (3)	−0.005 (3)
C5	0.052 (4)	0.061 (4)	0.033 (3)	0.005 (3)	0.016 (2)	−0.004 (3)

C6	0.055 (4)	0.064 (4)	0.045 (3)	0.008 (3)	0.017 (3)	0.007 (3)
C7	0.045 (4)	0.077 (4)	0.054 (4)	0.006 (3)	0.012 (3)	0.005 (3)
C8	0.065 (4)	0.058 (4)	0.053 (4)	0.004 (3)	0.026 (3)	0.002 (3)
C9	0.059 (4)	0.060 (4)	0.051 (4)	0.011 (3)	0.014 (3)	0.008 (3)
C10	0.049 (4)	0.070 (4)	0.049 (3)	0.006 (3)	0.013 (3)	−0.003 (3)
C11	0.124 (7)	0.067 (5)	0.104 (6)	−0.001 (4)	0.034 (5)	0.028 (4)
C12	0.056 (4)	0.058 (4)	0.055 (4)	−0.001 (3)	0.016 (3)	0.001 (3)
C13	0.079 (5)	0.089 (5)	0.048 (4)	0.002 (4)	0.018 (3)	0.001 (3)
C14	0.088 (6)	0.193 (9)	0.062 (5)	0.030 (7)	−0.007 (4)	−0.010 (6)

Geometric parameters (Å, °)

Re—O1	1.679 (4)	C5—C10	1.382 (7)
Re—N	2.189 (5)	C5—C6	1.393 (7)
Re—S1	2.2762 (16)	C6—C7	1.370 (8)
Re—S2	2.2833 (16)	C6—H6A	0.9300
Re—S3	2.3030 (16)	C7—C8	1.390 (8)
S2—C3	1.820 (6)	C7—H7A	0.9300
S1—C1	1.820 (6)	C8—C9	1.372 (8)
S3—C5	1.782 (6)	C9—C10	1.377 (8)
N—C4	1.489 (6)	C9—H9A	0.9300
N—C2	1.493 (7)	C10—H10A	0.9300
N—C12	1.509 (7)	C11—H11A	0.9600
O2—C8	1.376 (7)	C11—H11B	0.9600
O2—C11	1.416 (7)	C11—H11C	0.9600
C1—C2	1.498 (8)	C12—C13	1.536 (8)
C1—H1B	0.9700	C12—H12A	0.9700
C1—H1C	0.9700	C12—H12B	0.9700
C2—H2A	0.9700	C13—C14	1.486 (10)
C2—H2B	0.9700	C13—H13A	0.9700
C3—C4	1.497 (8)	C13—H13B	0.9700
C3—H3A	0.9700	C14—H14A	0.9600
C3—H3B	0.9700	C14—H14B	0.9600
C4—H4A	0.9700	C14—H14C	0.9600
C4—H4B	0.9700		
O1—Re—N	96.85 (18)	H4A—C4—H4B	108.2
O1—Re—S1	117.42 (14)	C10—C5—C6	118.4 (5)
N—Re—S1	83.14 (12)	C10—C5—S3	118.9 (5)
O1—Re—S2	119.65 (14)	C6—C5—S3	122.6 (4)
N—Re—S2	82.81 (11)	C7—C6—C5	120.0 (5)
S1—Re—S2	122.34 (6)	C7—C6—H6A	120.0
O1—Re—S3	104.45 (14)	C5—C6—H6A	120.0
N—Re—S3	158.59 (13)	C6—C7—C8	121.2 (6)
S1—Re—S3	85.19 (6)	C6—C7—H7A	119.4
S2—Re—S3	88.41 (6)	C8—C7—H7A	119.4
C3—S2—Re	102.7 (2)	C9—C8—O2	125.9 (6)
C1—S1—Re	103.7 (2)	C9—C8—C7	118.8 (6)
C5—S3—Re	110.64 (18)	O2—C8—C7	115.3 (6)
C4—N—C2	110.2 (5)	C8—C9—C10	120.4 (6)

C4—N—C12	111.8 (4)	C8—C9—H9A	119.8
C2—N—C12	107.4 (4)	C10—C9—H9A	119.8
C4—N—Re	108.7 (3)	C9—C10—C5	121.2 (6)
C2—N—Re	110.5 (3)	C9—C10—H10A	119.4
C12—N—Re	108.1 (4)	C5—C10—H10A	119.4
C8—O2—C11	117.4 (6)	O2—C11—H11A	109.5
C2—C1—S1	110.7 (5)	O2—C11—H11B	109.5
C2—C1—H1B	109.5	H11A—C11—H11B	109.5
S1—C1—H1B	109.5	O2—C11—H11C	109.5
C2—C1—H1C	109.5	H11A—C11—H11C	109.5
S1—C1—H1C	109.5	H11B—C11—H11C	109.5
H1B—C1—H1C	108.1	N—C12—C13	115.7 (5)
N—C2—C1	112.4 (5)	N—C12—H12A	108.4
N—C2—H2A	109.1	C13—C12—H12A	108.4
C1—C2—H2A	109.1	N—C12—H12B	108.4
N—C2—H2B	109.1	C13—C12—H12B	108.4
C1—C2—H2B	109.1	H12A—C12—H12B	107.4
H2A—C2—H2B	107.9	C14—C13—C12	111.9 (6)
C4—C3—S2	109.3 (4)	C14—C13—H13A	109.2
C4—C3—H3A	109.8	C12—C13—H13A	109.2
S2—C3—H3A	109.8	C14—C13—H13B	109.2
C4—C3—H3B	109.8	C12—C13—H13B	109.2
S2—C3—H3B	109.8	H13A—C13—H13B	107.9
H3A—C3—H3B	108.3	C13—C14—H14A	109.5
N—C4—C3	110.0 (5)	C13—C14—H14B	109.5
N—C4—H4A	109.7	H14A—C14—H14B	109.5
C3—C4—H4A	109.7	C13—C14—H14C	109.5
N—C4—H4B	109.7	H14A—C14—H14C	109.5
C3—C4—H4B	109.7	H14B—C14—H14C	109.5

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12B···O1	0.97	2.59	2.971 (7)	104

Fig. 1

Fig. 2

Fig. 3