

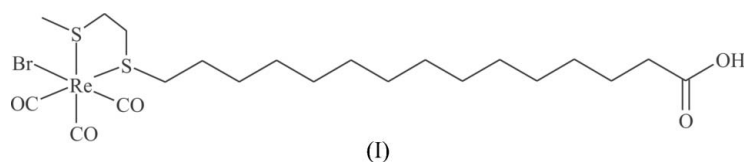
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Key indicators

Single-crystal X-ray study
 $T = 273$ K
Mean $\sigma(\text{C}-\text{C}) = 0.013$ Å
Disorder in main residue
 R factor = 0.061
 wR factor = 0.160
Data-to-parameter ratio = 15.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bromotricarbonyl{15-[2-(methylsulfanyl)ethyl-
sulfanyl]pentadecanoic acid- $\kappa^2\text{S,S}'$ }rhenium(I)The title compound, $[\text{ReBr}(\text{C}_{18}\text{H}_{36}\text{O}_2\text{S}_2)(\text{CO})_3]$, was synthe-
sized and characterized as a non-radioactive surrogate of a
novel Tc-containing fatty acid derivative prepared according
to the tricarbonyl/dithioether design with the objective of
developing new Tc-based radiopharmaceuticals for the non-
invasive diagnosis of myocardial metabolism. The Re chelate
contains the metal in the oxidation state +1 and is attached to
the terminal position of a fatty acid. The complex formation
was accomplished by a ligand exchange reaction using
 $[\text{NBu}_4]_2[\text{Re}(\text{CO})_3\text{Br}_3]$ as starting material.Received 21 June 2006
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Comment

The organometallic fragment $\text{fac}-[\text{M}(\text{CO})_3]^+$ ($M = \text{Tc}$ and Re)
was introduced as a versatile synthon for the conjugation of
biomolecules with technetium or rhenium (Alberto *et al.*, 1999;
Waibel *et al.*, 1999; Metzler-Nolte, 2001). $[\text{Tc}(\text{CO})_3\text{cp}]$ (cp =
cyclopentadienyl) and $[\text{Tc}(\text{CO})_3(\text{N}-\text{N})]$ ($\text{N}-\text{N}$ = azoimida-
zoles) were recently used for Tc-labelling of fatty acids (Lee
et al., 2004; Chu *et al.*, 2004). The highly lipophilic character of
these metal(I)-tricarbonyl units in contrast to the relatively
polar oxotechnetium(V) species makes it suitable for
mimicking lipophilic long-chain fatty acids. Owing to the
known tendency of the metal(I) center to interact strongly
with soft donor compounds, in addition to bidentate aromatic
Schiff base ligands (Jung *et al.*, 2002), dithioethers ($R-\text{S}-$
 $\text{CH}_2\text{CH}_2\text{S}-R$) are also exceedingly suitable for coordinating
the tricarbonylmethyl(I) unit. The two sulfur donor atoms
replace two bromides of the tricarbonylrhenium(I) precursor
 $[\text{NBu}_4]_2[\text{Re}(\text{CO})_3\text{Br}_3]$, whereas the third bromide substituent
remains in the coordination sphere of the metal(I) core and is
responsible for the compensation of the charge.In the molecular structure (Fig. 1) of the neutral mono-
nuclear complex (I), each Re^{I} atom is six-coordinated by one
bidentate dithioether ligand, three carbonyl ligands and a Br^-
anion, displaying an $\text{ReC}_3\text{S}_2\text{Br}$ octahedral geometry. The Br
atom and the carboxyl group are disordered over two posi-
tions. The major component has an occupation factor of
0.757 (5). The metal-ligand distances within the framework
are characterized by Re—C contacts ranging from 1.889 (14)
to 1.918 (11) Å, and Re—S and Re—Br contacts of 2.482 (3)
and 2.587 (2) Å, respectively [for the minor occupied site

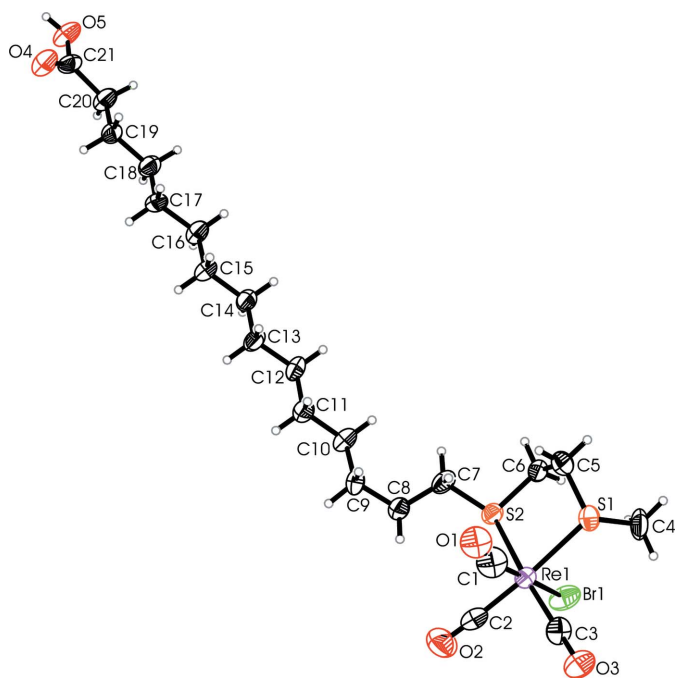


Figure 1
Perspective view of (I), showing 30% probability displacement ellipsoids. Only the major disorder component is shown.

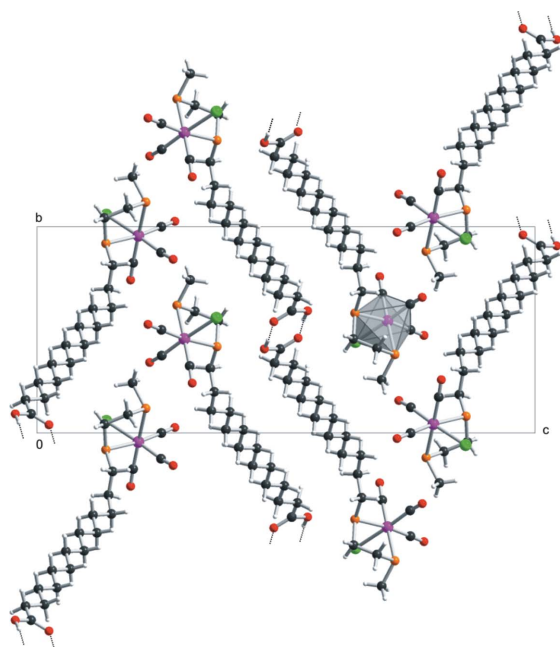


Figure 2
Arrangement of the molecules in the crystal structure, showing an antiparallel arrangement of the motif in the unit cell. The hydrogen bonds are indicated as dashed lines. One Re octahedron is highlighted.

$\text{Re1}-\text{C1}' = 1.896(10) \text{ \AA}$ and $\text{Re1}-\text{Br1}' = 2.522(6) \text{ \AA}$]. For clarity, Fig. 1 shows the major disorder component only. In the crystal structure, the molecules are arranged in a herringbone

pattern along the *b* axis, with the Re octahedra pointing towards each other. The Re atoms of adjacent molecules are arranged in a zigzag manner, leading to $\text{Re} \cdots \text{Re}$ distances of $6.792(11) \text{ \AA}$. As illustrated in Fig. 2, two molecules are interconnected *via* two symmetry-related hydrogen bonds between the carboxyl groups (Table 2), forming dimers in the crystal structure. Hydrophobic interaction between the chains leads to stable packing. As a consequence of the molecular arrangement, organic and organometallic areas can be distinguished. In an alternative description the crystal structure can be regarded as a stacked structure of layers consisting of dimers. The layers run parallel to the $(\bar{1} \bar{1} 18)$ and the $(\bar{1} 1 18)$ plane, stacked along the *c* axis, showing an *A-B-B-A* stacking motif.

Experimental

The fatty acid ligand 15-[[2-(methylthio)ethyl]thio]pentadecanoic acid (47 mg, 135 μmol) was dissolved in MeOH (5 ml) and added to a solution of the tricarbonylrhenium(I) precursor bis[tetra(*n*-butyl) ammonium]tribromotricarbonylrhenium(I) (100 mg, 130 μmol) in MeOH (1 ml). After stirring for 6 h at room temperature, the solvent was removed *in vacuo*. The residue was redissolved in dry THF (10 ml) and the resulting insoluble ammonium salt was filtered off. Purification of the residue was accomplished by column chromatography ($\text{CHCl}_3/\text{MeOH}$ 14:1); yield 71 mg (78%) of colorless waxy solid. Crystals of the complex suitable for X-ray single-crystal analysis were obtained by slow crystallization from a chloroform/hexane solution (3:2) at room temperature. Analysis calculated for $\text{C}_{21}\text{H}_{36}\text{BrO}_5\text{ReS}_2$ (698.76): C 36.10, H 5.19, S 9.18, Br 11.44%; found C 36.30, H 5.13, S 9.21, Br 11.60%.

Crystal data

$[\text{ReBr}(\text{C}_{18}\text{H}_{36}\text{O}_2\text{S}_2)(\text{CO})_3]$
 $M_r = 698.73$
Monoclinic, $P2_1/c$
 $a = 7.486(5) \text{ \AA}$
 $b = 12.041(8) \text{ \AA}$
 $c = 29.07(2) \text{ \AA}$
 $\beta = 90.349(16)^\circ$
 $V = 2620(3) \text{ \AA}^3$

$Z = 4$
 $D_x = 1.771 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
 $\mu = 6.35 \text{ mm}^{-1}$
 $T = 273(2) \text{ K}$
Block, colorless
 $0.45 \times 0.35 \times 0.25 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
 ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.076$, $T_{\text{max}} = 0.205$

9728 measured reflections
4364 independent reflections
3820 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.099$
 $\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.061$
 $wR(F^2) = 0.160$
 $S = 1.08$
4364 reflections
277 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0819P)^2 + 15.1703P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.017$
 $\Delta\rho_{\text{max}} = 2.89 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.98 \text{ e \AA}^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: $0.0031(4)$

Table 1

Selected geometric parameters (Å, °).

Re1—C2	1.889 (14)	S1—C5	1.805 (12)
Re1—C1	1.890 (9)	S2—C6	1.802 (11)
Re1—C3	1.918 (11)	S2—C7	1.818 (10)
Re1—S2	2.478 (3)	O2—C2	1.157 (15)
Re1—S1	2.482 (3)	O3—C3	1.154 (13)
Re1—Br1	2.587 (2)	O4—C21	1.228 (13)
O1—C1	1.134 (9)	O5—C21	1.306 (12)
S1—C4	1.776 (12)		
C2—Re1—C1	86.9 (8)	C2—Re1—Br1	90.9 (4)
C2—Re1—C3	89.8 (5)	C1—Re1—Br1	177.2 (7)
C1—Re1—C3	89.2 (8)	C3—Re1—Br1	92.4 (3)
C2—Re1—S2	92.5 (4)	S1—Re1—Br1	92.39 (9)
C1—Re1—S2	97.8 (7)	O1—C1—Re1	164 (2)
C3—Re1—S2	172.7 (3)	C4—S1—Re1	112.5 (4)
C2—Re1—S1	175.5 (3)	C5—S1—Re1	102.1 (4)
C1—Re1—S1	89.7 (7)	C6—S2—C7	102.4 (5)
C3—Re1—S1	93.0 (3)	O2—C2—Re1	176.1 (12)
S2—Re1—S1	85.07 (9)	O3—C3—Re1	178.8 (10)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5A ⁱ ···O4 ⁱ	0.82	1.86	2.681 (11)	174

Symmetry code: (i) $-x - 4, -y, -z$.

The atoms of disordered carbonyl groups were refined isotropically. All H atoms were positioned geometrically and refined as

riding, with C—H = 0.96 and 0.97 Å, O—H = 0.82 Å, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$ ($1.5U_{\text{eq}}$ for OH and methyl groups). The highest peak and the deepest hole in the final difference Fourier map are located 1.02 and 1.05 Å from Re, respectively.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*; 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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