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Two mononuclear Tc complexes: [2,2′-(3-phenylpropylimino)- and [2,2′-(propylimino)bis(ethanethiolato)](4-methoxybenzenethiolato)oxidotechnate(V)

Franziska Emmerling,[a] Werner Kraus,[a]* Bernhard Noll,[b] Steffi Noll[b] and Hans-Jürgen Pietzsch[b]

[a]Bundesanstalt für Materialforschung und -prüfung, Richard-Willstätter-Strasse 11, D-12489 Berlin, Germany, and [b]Forschungszentrum Rossendorf, Institut für Radiopharmazie, Postfach 510119, D-01314 Dresden, Germany
Correspondence e-mail: w.kraus@bam.de

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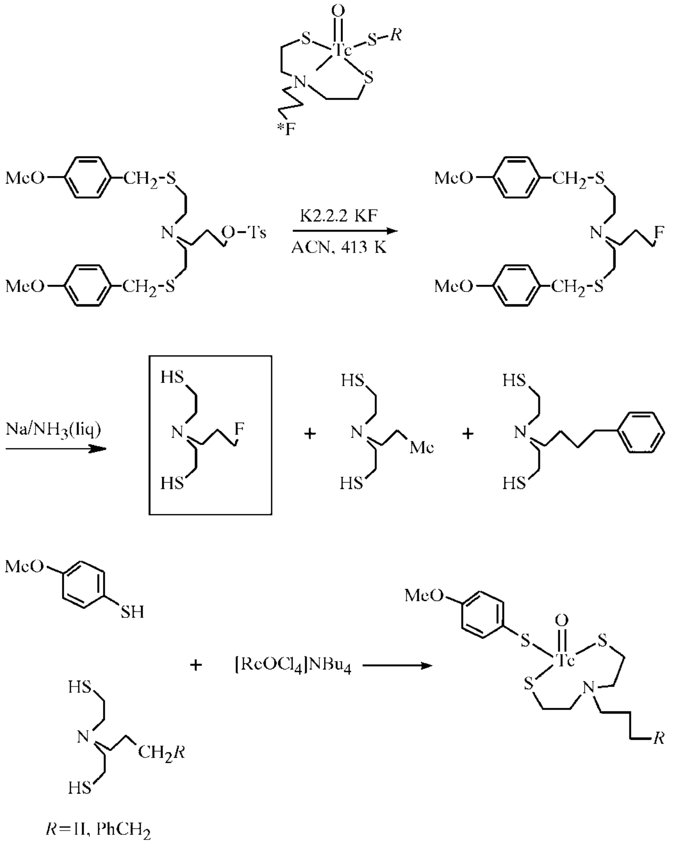
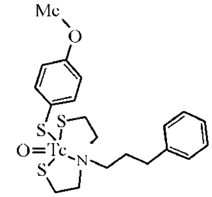
The molecular structures of the two mononuclear title complexes, namely (4-methoxybenzenethiolato-*κS*)oxido[2,2′-(3-phenylpropylimino)bis(ethanethiolato)-$\kappa^3 S,N,S'$]technetium(V), $[Tc(C_{14}H_{21}NS_2)(C_7H_7OS)O]$, (I), and (4-methoxybenzenethiolato-*κS*)oxido[2,2′-(propylimino)bis(ethanethiolato)-$\kappa^3 S,N,S'$]technetium(V), $[Tc(C_7H_{15}NS_2)(C_7H_7OS)O]$, (II), exhibit the same coordination environment for the central Tc atoms. The atoms are five-coordinated ($TcNOS_3$) with a square-pyramidal geometry comprising a tridentate 2,2′-(3-phenylpropylimino)bis(ethanethiolate) or 2,2′-(propylimino)bis(ethanethiolate) ligand, a 4-methoxybenzenethiolate ligand and an additional oxide O atom. Intermolecular C—H⋯O and C—H⋯S hydrogen bonds between the monomeric units result in two-dimensional layers with a parallel arrangement.

Comment

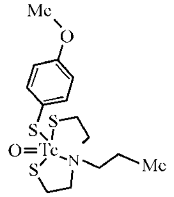
Recently, a new method has been described that allows the use of metal complexes as a prosthetic group in ^{18}F labelling of biologically relevant molecules (Noll *et al.*, 2002). The principle is based on labelling a tridentate dithiole ligand with ^{18}F and combining it with a monodentate thiole ligand to form mixed-ligand technetium complexes (see scheme). To understand the reaction route, a nonradioactive fluorine model compound was prepared and all by-products obtained were characterized by X-ray crystal structure analysis. We describe here only the metal complexes of the by-products, *viz*. the title compounds, (I) and (II).

The molecular structures of (I) and (II) reveal that they are neutral square-pyramidal mononuclear complexes (Figs. 1 and 2). Similar Re complexes are currently under study for various applications (Bouziotis *et al.*, 1999; 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; Nock, Maina, Tisato, Papadopoulos *et al.*, 1999; Nock, Maina, Tisato, Raptopoulou *et al.*, 1999; Papadopoulos *et al.*, 1999; Tsoukalas *et al.*, 1999). In the case of the title compounds, the Tc atom is coordinated by two S atoms and an N atom from the tridentate ligand, another S atom provided by the 4-methoxybenzenethiolate ligand and an additional oxide O atom to complete the coordination environment. The cation environments in both structures are comparable, with axial Tc—O distances of 1.657 (6) Å in (I) and 1.671 (3) Å in (II), Tc—N distances of 2.213 (6) Å in (I) and 2.201 (4) Å in (II), and Tc—S bond lengths in the ranges 2.241 (3)–2.308 (3) Å in (I) and 2.2801 (19)–2.3093 (19) Å in (II). The values mentioned above are in good agreement with those reported in the Cambridge Structural Database (Version 5.27; Allen, 2002; Tc—O = 1.654–1.670 Å, mean 1.663 Å; Tc—N = 1.996–2.259 Å, mean 2.194 Å; Tc—S = 2.280–2.359 Å, mean 2.304 Å). The Tc1—S3—C5 angles between the methoxyphenyl group and the central Tc atom are nearly similar [109.6 (3)° in (I) and 109.2 (2)° in (II)], whereas the S2—Tc1—S3—C5 torsion





(I)



(II)

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angles of −164.0 (4) and 45.5 (2)° in (I) and (II), respectively, indicate opposite positions of the methoxyphenyl group.

Analysis of the crystal packing of the title complexes reveals that the monomeric units are linked *via* nonclassical C—H···O hydrogen bonds in complexes (I) and (II), and C—H···S hydrogen bonds in complex (II) only, resulting in a two-dimensional layer structure. Thus, each complex is linked to four others, forming a sheet parallel to (110). The relevant hydrogen-bonding geometries and symmetry codes are listed in Tables 2 and 4.

As illustrated in Figs. 3 and 4, the head-to-tail arrangement of the molecules within the layers leads to a zigzag formation of the Tc atoms, along the *a* axis in the crystal structure of compound (I) and along the *b* axis in the case of compound (II), with Tc···Tc distances of 6.760 (13) and 7.042 (16) Å in (I) and 6.102 (4) Å in (II). Due to the larger phenylpropyl-

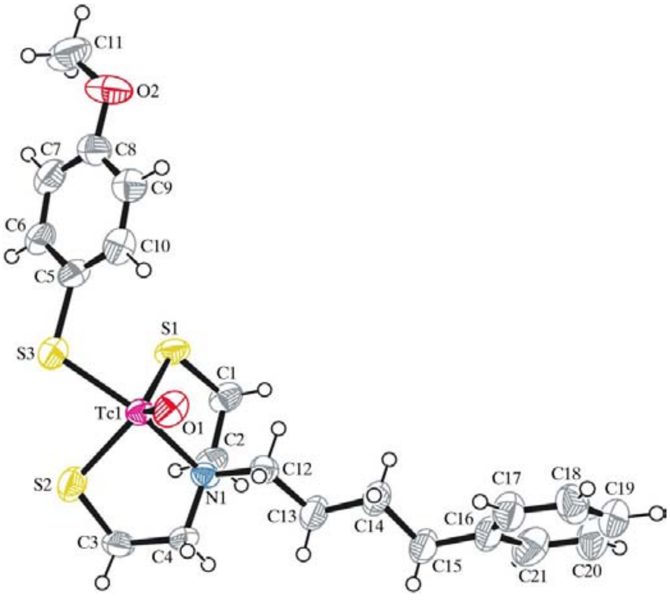

Figure 1
The molecular structure of the ‘3+1’ Tc complex (I), showing the atomic labelling of the asymmetric unit and the coordination environment. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

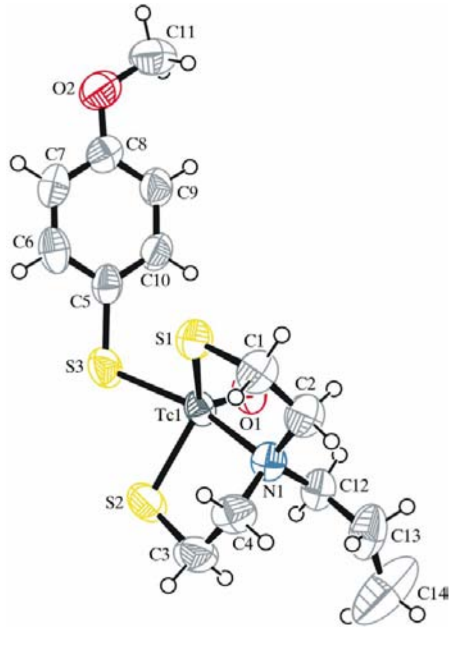

Figure 2
The molecular structure of the ‘3+1’ Tc complex (II), showing the atomic labelling of the asymmetric unit and the coordination environment. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

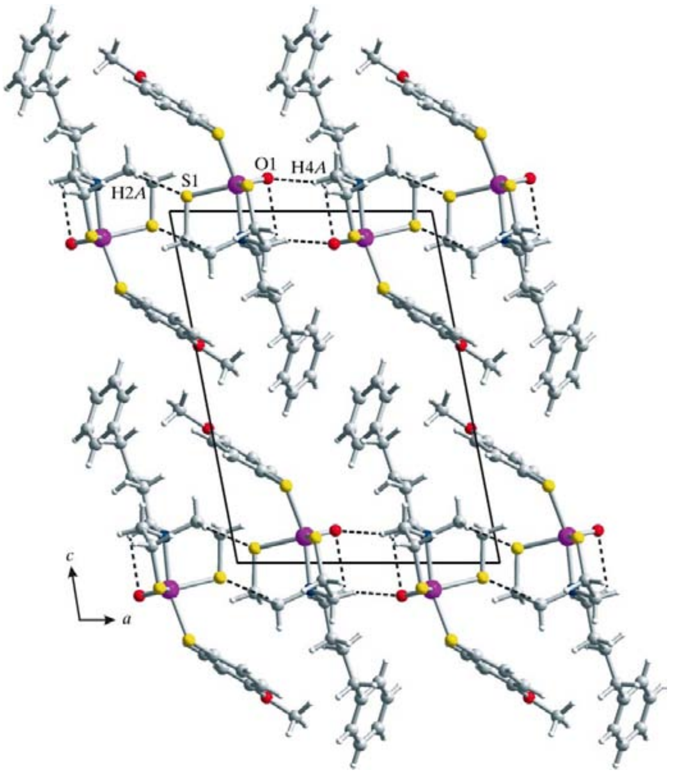

Figure 3
The two-dimensional supramolecular structure of complex (I), formed *via* C—H···O hydrogen bonds (dashed lines) between the molecules.

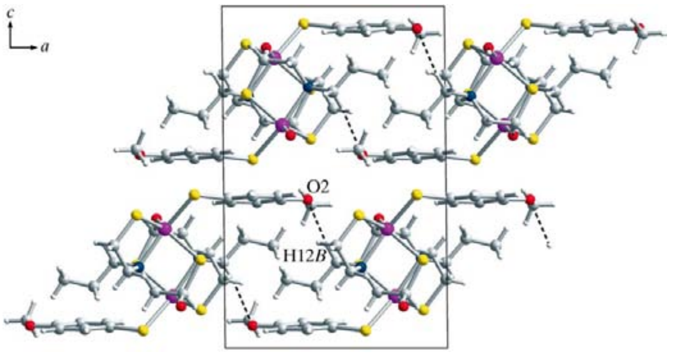

Figure 4
The two-dimensional supramolecular structure of complex (II), formed *via* C—H···O and C—H···S hydrogen bonds (dashed lines) between the molecules.

imine ligand, the distance between adjacent sheets is larger in (I) than in (II); in either case, no π–π interactions are observed.

Experimental

The synthesis started with the preparation of the tridentate ligand containing both the sulfur-protecting groups and tosyl as leaving group. In the next step, fluorine was introduced by nucleophilic substitution in acetonitrile with Kryptofix 2.2.2 at 413 K. Subsequently, both sulfur-protecting benzyl groups were split off by reductive cleavage in liquid ammonia and metallic sodium. This reaction was accompanied by rearrangement of the ligand molecule, and besides the favoured fluorinated species two by-products were formed (see reaction scheme in *Comment*). Without further purification, the fluorinated tridentate ligand was combined with the monodentate *p*-methoxybenzenethiol ligand as model compound and Re or Tc in the oxidation state +5 to give a '3+1' complex (see reaction scheme in *Comment*). The Tc complexes were separated out by column chromatography on silica gel with dichloromethane as eluent. The fractions were collected and evaporated to dryness. Crystals of the metal complexes were grown from ethanol. We describe here only the metal complexes of the by-products.

Compound (I)

Crystal data

$[Tc(C_{14}H_{21}NS_2)(C_7H_7OS)O]$
M_r = 520.62
Monoclinic, $P2_1$
a = 10.885 (7) Å
b = 7.247 (4) Å
c = 14.885 (7) Å
β = 100.913 (8)°
V = 1152.9 (11) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.91 mm^{-1}
T = 273 (2) K
0.45 × 0.39 × 0.15 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.656, $T_{\max}$ = 0.872
6818 measured reflections
4523 independent reflections
3581 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.144
S = 1.02
4523 reflections
236 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{\max}$ = 1.57 e Å^{-3}
$\Delta\rho_{\min}$ = −0.81 e Å^{-3}
Absolute structure: Flack (1983), with 1730 Friedel pairs
Flack parameter: 0.49 (3)

Table 1
Selected bond lengths (Å) for (I).

Tc1—O1	1.657 (6)	Tc1—S1	2.279 (3)
Tc1—N1	2.213 (6)	Tc1—S3	2.308 (3)
Tc1—S2	2.241 (3)		

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2A···S1$^{\rm i}$	0.97	2.78	3.650 (9)	150
C4—H4A···O1$^{\rm ii}$	0.97	2.52	3.164 (13)	124

Symmetry codes: (i) $-x, y - \frac{1}{2}, -z$; (ii) $-x + 1, y - \frac{1}{2}, -z$.

Compound (II)

Crystal data

$[Tc(C_7H_{15}NS_2)(C_7H_7OS)O]$
M_r = 430.51
Monoclinic, $P2_1/n$
a = 10.610 (7) Å
b = 10.356 (7) Å
c = 16.296 (11) Å
β = 90.574 (15)°
V = 1790 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.16 mm^{-1}
T = 273 (2) K
0.15 × 0.09 × 0.02 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.879, $T_{\max}$ = 0.978
10232 measured reflections
4031 independent reflections
1809 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.092

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.095
S = 0.86
4031 reflections
190 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.92 e Å^{-3}
$\Delta\rho_{\min}$ = −0.60 e Å^{-3}

Table 3
Selected bond lengths (Å) for (II).

Tc1—O1	1.671 (3)	Tc1—S1	2.2856 (19)
Tc1—N1	2.201 (4)	Tc1—S3	2.3093 (19)
Tc1—S2	2.2801 (19)		

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3B···O1$^{\rm i}$	0.97	2.53	3.464 (7)	162
C12—H12A···O2$^{\rm ii}$	0.97	2.58	3.396 (7)	142

Symmetry codes: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x + 1, y, z$.

Compound (I) crystallizes in the noncentrosymetric space group $P2_1$ and was refined as an inversion twin with a Flack (1983) parameter of 0.48 (3). Restraints were used for the displacement parameters of four C atoms (C13–C16).

For compound (II), the low $N_{\rm obs}/N_{\rm tot}$ ratio is the inescapable result of the poor quality of the crystals available; in various trials neither better crystals nor resulting data sets could be obtained. This result was unexpected, since comparable Tc compounds investigated by our group tend to build good quality crystals.

All H atoms in both structures were included using a riding model, with C—H = 0.93–0.97 Å and $U_{\rm iso}$(H) = 1.2–1.5$U_{\rm eq}$(C).

For both compounds, 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*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3060). Services for accessing these data are described at the back of the journal.

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