Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (Walker & Stuart, 1983)
$T_{\min} = 0.090$, $T_{\max} = 0.115$
3230 measured reflections
2888 independent reflections

1732 reflections with $I > 3\sigma(I)$
$R_{\text{int}} = 0.049$
$\theta_{\max} = 26.32°$
$h = -10 \rightarrow 0$
$k = 0 \rightarrow 18$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: 3.2%

Refinement

Refinement on F
$R = 0.030$
$wR = 0.033$
$S = 0.972$
1732 reflections
212 parameters
H-atom coordinates refined
$w = 4F^2/[\sigma^2(I) + (0.04F^2)^2]$
$(\Delta/\sigma)_{\max} = 0.03$

$\Delta\rho_{\max} = 0.724$ e Å^{-3}
$\Delta\rho_{\min} = 0.000$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 4.584×10^{-9}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Re—C1	1.89 (1)	O5—C12	1.30 (1)
Re—C2	1.88 (1)	O6—C12	1.21 (1)
Re—C3	1.88 (1)	N—C9	1.34 (1)
Re—C4	2.290 (9)	N—C10	1.45 (1)
Re—C5	2.313 (9)	C4—C5	1.39 (1)
Re—C6	2.297 (8)	C4—C8	1.42 (1)
Re—C7	2.291 (8)	C5—C6	1.39 (1)
Re—C8	2.276 (8)	C6—C7	1.39 (1)
Re—Cnt	1.958	C7—C8	1.43 (1)
O1—C1	1.16 (1)	C8—C9	1.48 (1)
O2—C2	1.17 (1)	C10—C11	1.52 (1)
O3—C3	1.16 (1)	C11—C12	1.51 (1)
O4—C9	1.24 (1)		
C1—Re—C2	91.0 (5)	Re—C3—O3	177.0 (1)
C1—Re—C3	87.8 (5)	C9—N—C10	122.3 (7)
C1—Re—C8	157.6 (4)	O4—C9—N	121.6 (8)
C2—Re—C3	88.0 (5)	O4—C9—C8	120.5 (7)
C2—Re—C8	101.2 (4)	N—C9—C8	117.8 (7)
C3—Re—C8	111.1 (4)	N—C10—C11	111.9 (7)
C4—Re—C5	35.1 (3)	C10—C11—C12	112.5 (7)
C4—Re—C8	36.1 (3)	O5—C12—O6	123.5 (8)
C5—Re—C6	35.2 (3)	O5—C12—C11	113.1 (7)
C6—Re—C7	35.3 (3)	O6—C12—C11	123.4 (7)
C7—Re—C8	36.4 (3)	Cnt—Re—C1	126.5
Re—C1—O1	176 (1)	Cnt—Re—C2	124.4
Re—C2—O2	176.5 (9)	Cnt—Re—C3	127.1

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *SDP* (B. A. Frenz & Associates Inc., 1982). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: DU1167). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Anderson, G. W., Zimmerman, J. E. & Callahan, F. M. (1964). *J. Am. Chem. Soc.* **86**, 1839–1842.
B. A. Frenz & Associates Inc. (1982). *SDP Structure Determination Package*. College Station, Texas, USA.
Bodanszky, M. (1984). In *Principles of Peptide Synthesis*. New York: Springer-Verlag.
Bolton, A. E. & Hunter, W. M. (1973). *Biochem. J.* **133**, 529–539.
Enraf–Nonius (1977). *CAD*-4 *Operations Manual*. Enraf–Nonius, Delft, The Netherlands.
Gorfti, A., Salmain, M., Jaouen, G., McGlinchey, M. J., Bennouna, A. & Mousser, A. (1996). *Organometallics*, **15**, 142–151.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.
Means, G. E. & Feeney, R. E. (1990). *Bioconjug. Chem.* **1**, 2–12.
Meyer, O., Arif, A. M. & Gladysz, J. A. (1995). *Organometallics*, **14**, 1844–1849.
Salmain, M., Gunn, M., Gorfti, A., Top, S. & Jaouen, G. (1994). *Bioconjug. Chem.* **4**, 425–433.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.
Zachariasen, W. H. (1967). *Acta Cryst.* A**23**, 558–564.

Acta Cryst. (1997). C**53**, 449–451

Epimer B of Tetraphenylarsonium (Mercaptoacetylalanylglycylglycinato-*N*,*N'*,*N''*,*S*)oxotechnetate(V) (^{99}Tc) Chloroform Solvate

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Abstract

In the title compound, $(C_{24}H_{20}As)[TcO(C_9H_{11}N_3O_5S)]$.$CHCl_3$, technetium is coordinated to three amide N atoms and one S atom which form a square pyramid,

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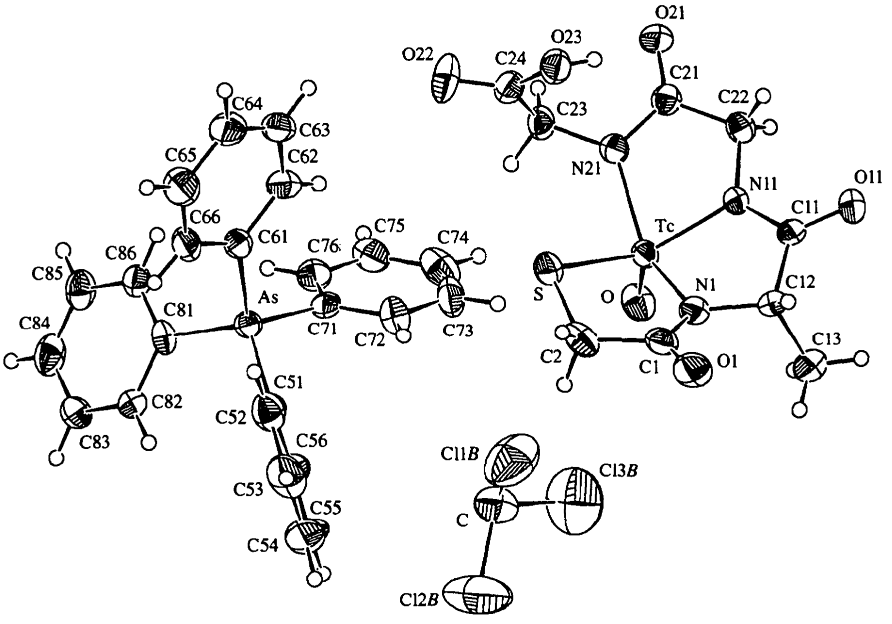
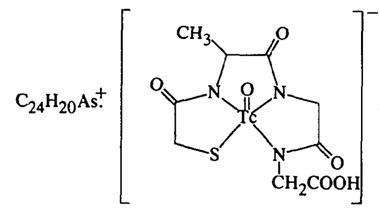


Fig. 1. *ZORTEP* (Zsolnai & Pritzkow, 1994) drawing of the title molecule showing the atomic numbering scheme. Ellipsoids are shown at the 40% probability level.

with the oxo group occupying the apical position such that the Tc atom lies 0.771 (5) Å above the least-squares basal plane. The methyl group adopts a *syn* configuration with respect to the oxo–metal group. The chloroform solvate molecule exhibits site occupation disorder with three positions for the Cl atoms.

Comment

The title molecule, (I), has a square-pyramidal arrangement around the Tc atom, with the oxo group occupying the apical position. The three N atoms and the S atom lie in a plane with a maximum deviation of 0.075 (6) Å. The Tc—O distance of 1.657 (5) Å is comparable with that in other monooxo complexes (Mahmood, Halpin, Baidoo, Sweigart & Lever, 1991). The mean value of the Tc—N bond length [2.002 (16) Å] is in the normal range for sp^2-hybridized N atoms. Distances and angles in the tetraphenylarsonium moiety are within normal ranges (Allen *et al.*, 1987). The deepest hole and highest peak from the difference Fourier synthesis after refinement are found between the disordered Cl atoms.



(I)

The atoms in the chloroform solvate molecule have high disorder and loss of this molecule is responsible for the deterioration of the crystal with time (crystals become opaque). The cations and anions are arranged in double chains along the **c** direction. The O23 atom forms an intramolecular hydrogen bond with the amino N21 atom and a weaker hydrogen bond with the carbonyl O21 atom (see Table 2). These hydrogen bonds determine the orientation of the O22 atom. Carbon–oxygen and carbon–sulfur distances in C23—H23*B*···O21 and C23—H23*A*···S [C23···O21 2.754 (9) and C23···S 3.214 (8) Å] are shorter than the sums of the van der Waals radii and could be classified as possible intramolecular contacts.

Weak intermolecular C—H···O contacts join the tetraphenylarsonium cation with the technetium complex ligands (see Table 2).

Experimental

The title compound was prepared from $NH_4{}^{99}TcO_4$ (spiked with $NH_4{}^{99m}TcO_4$), mercaptoacetyl-DL-alanylglycylglycine and sodium dithionite, dissolved in a phosphate buffer at pH 12. The technetium chelate was precipitated by the addition of tetraphenylarsonium chloride and recrystallized from an MeOH–$CHCl_3$ (9:1) solution.

Crystal data

$(C_{24}H_{20}As)[TcO(C_9H_{11}N_3O_5S)].CHCl_3$	Mo $K\alpha$ radiation
	$\lambda = 0.71073$ Å
$M_r = 890.89$	Cell parameters from 24 reflections
Monoclinic	
$P2_1/n$	$\theta = 10$–$12°$

$a = 9.484\ (5)$ Å
$b = 10.949\ (7)$ Å
$c = 35.74\ (2)$ Å
$\beta = 93.87\ (4)°$
$V = 3703\ (4)$ Å^3
$Z = 4$
$D_x = 1.598$ Mg m^{-3}
$D_m = 1.5$ Mg m^{-3}
D_m measured by flotation in aqueous $CdCl_2$ solution

$\mu = 1.595$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.76 × 0.16 × 0.04 mm
Orange

Data collection

Stoe Stadi-4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (*EMPIR*; Stoe & Cie, 1988*b*)
$T_{\min} = 0.711$, $T_{\max} = 0.938$
13 660 measured reflections
6491 independent reflections

3391 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0580$
$\theta_{\max} = 25°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 13$
$l = -42 \rightarrow 42$
3 standard reflections
frequency: 60 min
intensity decay: 1.2%

Refinement

Refinement on F^2
$R(F) = 0.0489$
$wR(F^2) = 0.1935$
$S = 1.006$
6452 reflections
499 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0632P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.007$
$\Delta\rho_{\max} = 0.78$ e Å^{-3}
$\Delta\rho_{\min} = -0.52$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Tc—O	1.657 (5)	N11—C22	1.434 (9)
Tc—N1	2.000 (6)	C11—O11	1.235 (9)
Tc—S	2.278 (2)	C11—C12	1.52 (1)
Tc—N11	1.974 (6)	C12—C13	1.52 (1)
Tc—N21	2.031 (6)	N21—C21	1.365 (9)
N1—C1	1.35 (1)	N21—C23	1.452 (9)
N1—C12	1.473 (9)	C21—O21	1.233 (9)
C1—O1	1.223 (9)	C21—C22	1.51 (1)
C1—C2	1.51 (1)	C23—C24	1.52 (1)
C2—S	1.806 (8)	C24—O22	1.201 (9)
N11—C11	1.345 (9)	C24—O23	1.314 (9)
N11—Tc—N21	77.9 (2)	Tc—N11—C11	119.3 (5)
S—Tc—N21	89.8 (2)	C11—N11—C22	121.4 (6)
S—Tc—N11	134.6 (2)	N11—C11—C12	113.8 (6)
N1—Tc—N21	138.6 (3)	N11—C11—O11	125.2 (6)
N1—Tc—N11	78.8 (3)	O11—C11—C12	121.0 (6)
N1—Tc—S	82.9 (2)	N1—C12—C11	107.4 (6)
O—Tc—N21	109.7 (3)	C11—C12—C13	112.1 (6)
O—Tc—N11	113.9 (3)	N1—C12—C13	111.8 (6)
O—Tc—S	111.4 (2)	Tc—N21—C23	125.5 (4)
O—Tc—N1	110.9 (3)	Tc—N21—C21	117.3 (5)
Tc—N1—C12	115.3 (4)	C21—N21—C23	116.9 (6)
Tc—N1—C1	125.2 (5)	N21—C21—C22	113.3 (6)
C1—N1—C12	118.3 (6)	N21—C21—O21	125.3 (7)
N1—C1—C2	114.2 (7)	O21—C21—C22	121.4 (7)
N1—C1—O1	124.8 (7)	N11—C22—C21	109.0 (6)
O1—C1—C2	121.0 (7)	N21—C23—C24	117.4 (6)
C1—C2—S	112.3 (6)	C23—C24—O23	116.1 (6)
Tc—S—C2	99.9 (3)	C23—C24—O22	121.5 (7)
Tc—N11—C22	119.1 (5)	O22—C24—O23	122.4 (7)
N11—Tc—N21—C21	16.3 (5)	O—Tc—N1—C1	−103.1 (6)
O—Tc—N21—C21	−95.0 (5)	O—Tc—N1—C12	90.1 (5)
S—Tc—N21—C23	−33.6 (5)	S—Tc—N1—C1	7.1 (6)
O—Tc—N21—C23	79.1 (6)	N1—C1—C2—S	−22.3 (9)
N1—Tc—N11—C11	14.6 (5)	N11—C11—C12—N1	−12.1 (8)
O—Tc—N11—C11	−93.5 (6)	O11—C11—C12—N1	167.6 (6)
O—Tc—N11—C22	90.7 (6)	N21—C21—C22—N11	1.4 (9)
O—Tc—S—C2	94.2 (3)	N21—C23—C24—O23	17 (1)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
O23—H23···N21	2.41	2.788 (8)	109
O23—H23···O21	2.78	3.461 (7)	141
C63—H63···O22	2.66	3.347 (10)	132
C74—H74···O11$^{\rm i}$	2.69	3.357 (11)	129
C66—H66···O11$^{\rm ii}$	2.22	3.124 (10)	162
C86—H86···O21$^{\rm iii}$	2.44	3.229 (9)	142.1

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

A scan width of 1.2° plus $\alpha_1 - \alpha_2$ divergence and a variable scan rate in the range 0.5–2.0 s per step was used. Empirical absorption corrections based on ψ scans and corrections for linear decay and for Lp were applied. The structure was solved using direct methods. All non-H atoms were refined anisotropically except for those of the disordered chloroform solvate molecule. H atoms were located on ideal molecular geometries and refined using a riding model. The C—Cl distance in the disordered molecule was restrained to 1.74 Å and the occupation factor of the disordered Cl atoms was fixed at 0.33. The Cl atoms were restrained to have the same U^{ij} components within 0.01 Å^2 in the direction of the C—Cl bond. Components of the anisotropic displacement factors of the Cl atoms were restrained to be equal within 0.02 Å^2 when the Cl atoms were closer than 0.7 Å.

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1994). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: NA1260). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A. & Polidori, G. (1994). *J. Appl. Cryst.* **27**, 435.

Mahmood, A., Halpin, W. A., Baidoo, K. E., Sweigart, D. A. & Lever, S. Z. (1991). *Acta Cryst.* C**47**, 254–257.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Stoe & Cie (1988*a*). *DIF4. Diffractometer Control Program.* Version 6.2. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1988*b*). *EMPIR. Empirical Absorption Correction Program.* Version 1.2. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1992). *REDU4. Data Reduction Program.* Version 7.03. Stoe & Cie, Darmstadt, Germany.

Zsolnai, L. & Pritzkow, H. (1994). *ZORTEP. ORTEP Program for PC.* University of Heidelberg, Germany.