

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1971). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1088). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 838–840

(*meso*-4,8-Diaza-3,9-dimethyl-6,6-trimethyleneundecane-2,10-dione dioximato-*N,N',N'',N'''*)oxotechnetium(V), [TcO(C₁₄H₂₅N₄O₂)]

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(Received 12 June 1995; accepted 12 October 1995)

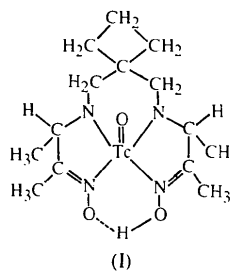
Abstract

The title compound was synthesized and analyzed by X-ray diffraction, in addition to IR, NMR, visible–UV and mass spectral studies. The coordination geometry about the Tc^V atom is five-coordinate square pyramidal, with four N atoms in equatorial positions and an O atom in the axial position. The Tc=O double-bond distance is 1.664(5) Å. The two amide Tc–N bond lengths are shorter than the two oxime Tc–N bond lengths. The central six-membered ring has a boat conformation with the Tc-bonded O atom ‘hanging’ above. The

intramolecular hydrogen-bond length between the two O atoms of the oxime groups is 2.432(9) Å. The cyclobutyl C atoms are, more or less, in a square plane.

Comment

A large number of ⁹⁹TcO–tetradentate amine oxime complexes have been shown to be neutral, lipophilic and able to cross the intact blood–brain barrier (Troutner, Volkert, Hoffman & Holmes, 1984; Volkert, Hoffman, Seger, Troutner & Holmes, 1984; Jurisson *et al.*, 1986, 1987). Of these, HM-PAO (3,6,6,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime), the main component of CeretecTM (Amersham Inc., England), has been used widely in nuclear medicine for efficacious cerebral perfusion imaging. However, it has been realized that there is a vital defect regarding *in vitro* instability (Hung, Corlija, Volkert & Holmes, 1988). Recently, another potential brain-imaging agent, CB-PAO (4,8-diaza-3,9-dimethyl-6,6-trimethyleneundecane-2,10-dione dioxime) was proposed (Colombo *et al.*, 1989). ^{99m}Tc–CB-PAO showed higher *in vitro* stability and lipophilicity than ^{99m}Tc–HM-PAO (Bacciottini *et al.*, 1990). For a better understanding of these facts, it is of great interest to study the coordination pattern of the ⁹⁹Tc–CB-PAO crystal structure. This is the first time that a single crystal of a Tc complex of the *meso*-CB-PAO isomer, (I), has been isolated and the chemical bonding of Tc with CB-PAO examined.



X-ray crystallographic analysis showed the title crystal to consist of a mononuclear Tc complex. By referring to the N–Tc–N and O–Tc–N angles in Table 2, it can be seen that the coordination geometry about the Tc^V ion is five-coordinate distorted square pyramidal, with an O atom at the apex and four N atoms in the basal plane. The geometric parameters of TcN₄O in the present structure are comparable with those in [Tc^VO(pnao-3H)] [pnao-3H is 3,3'-(1,3-propanediyl-di-imino)bis(3-methyl-2-butanone oximato) (Fair, Troutner, Schlemper, Murmann & Hoppe, 1984)]. The Tc=O bond distance of 1.664(5) Å is somewhat shorter, compared with the values 1.670(4)–1.682(5) Å for mono(oxo)technetium(V)–tetradentate propylene amine oxime derivatives (Fair *et al.*, 1984; Jurisson *et al.*, 1986, 1987). The IR spectrum showed the Tc=O stretch at 931 cm⁻¹. This is at the high energy end of the

range observed for similar mono(oxo)technetium species [908–934 cm^{-1} (Fair *et al.*, 1984; Jurisson *et al.*, 1986, 1987)].

The four basal N atoms are coplanar to within 0.009 (10) Å, with the Tc atom lying 0.683 (3) Å above their least-squares plane. The N-bonded C atoms are coplanar within 0.04 (1) Å and intersect the basal N_4 plane at an angle of 1.3 (2)°. The plane formed by atoms C11, C12 and C13 is almost perpendicular [90.1 (5)°] to that formed by the cyclobutyl C atoms. The cyclobutyl C—C bond lengths range from 1.518 (16) to 1.545 (12) Å and their bond angles range from 88.7 (6) to 90.2 (7)°. The central six-membered ring containing the propylene group has a boat conformation. The monomeric TcO–*meso*-CB-PAO complex has apparently a boat form only, but dimeric TcO–*meso*-HM-PAO has two kinds of conformation, *i.e.* boat and chair forms (Jurisson *et al.*, 1986). The two amine Tc—N bond lengths are 1.917 (6) Å, which are shorter than the two oxime Tc—N bond lengths [2.075 (6) and 2.087 (7) Å]. The visible–UV spectrum exhibited an intense band at *ca* 294 nm, which was attributed to a ligand-to-metal charge-transfer transition, with a shoulder at *ca* 356 nm. The angles Tc—N3—C3 and Tc—N4—C4 are 119.3 (5) and 117.3 (5)°, respectively. The amine oxime ligand loses two amine protons and one oxime proton on coordination, resulting in a neutral complex with an intramolecular hydrogen bond [2.432 (9) Å] between the two O atoms of the oxime groups.

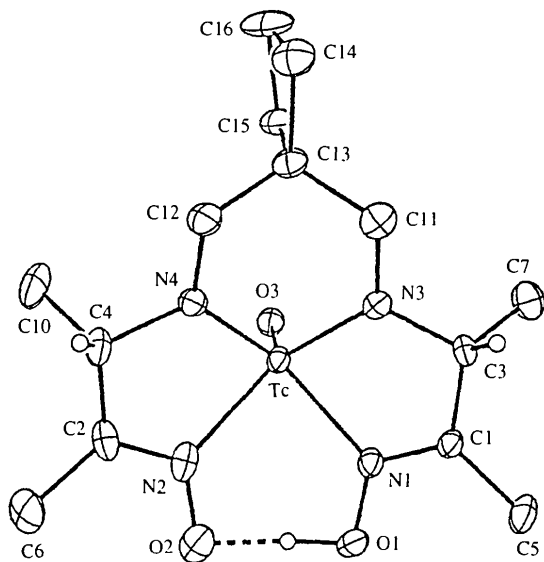


Fig. 1. A perspective view of the title molecule showing the atom-numbering scheme and excluding the H atoms attached to the outer C atoms. The displacement ellipsoids are drawn at the 50% probability level (SHELXTL-Plus; Sheldrick, 1986).

Experimental

The ligand 4,8-diaza-3,9-dimethyl-6,6-trimethyleneundecane-2,10-dione dioxime (CB-PAO) was synthesized according

to the method described in the literature (Deutsch, 1990). Fractional crystallization from acetonitrile and ethyl acetate (Neirincx *et al.*, 1987) provided the *meso* diastereoisomer (yield 35%, m.p. 428–429 K). Stereoisomeric purity was confirmed using ^{13}C NMR (d_6 -DMSO). Because of the symmetry, the three cyclobutyl CH_2 groups of the *meso* isomer yield three ^{13}C NMR signals (at *ca* 15.182, 28.096 and 28.266 p.p.m.), but only two signals for the *d,l* isomer. $^{99}\text{TcO-meso-CB-PAO}$ was prepared by the reduction of pertechnetate with stannous ion in the presence of ligand (Jurisson *et al.*, 1986). Analysis: calculated for $\text{C}_{14}\text{H}_{25}\text{N}_4\text{O}_3\text{Tc}$ C 42.42, H 6.31, N 14.14%; found C 42.40, H 6.41, N 14.05%. FAB-MS spectrum (positive ion mode): 397 a.m.u. for $(M+1)^+$. ^1H NMR (CDCl_3): δ 1.4766 (6H, *d*, Me), 2.2560 (6H, *s*, Me), 3.1243 and 3.5674 (4H, *d*, CH_2N), 4.3161 p.p.m. (2H, *q*, CH).

Crystal data

[TcO($\text{C}_{14}\text{H}_{25}\text{N}_4\text{O}_2$)]
 $M_r = 395.37$
 Monoclinic
 $P2_1/c$
 $a = 7.4275$ (20) Å
 $b = 18.2382$ (24) Å
 $c = 12.4692$ (14) Å
 $\beta = 90.743$ (16)°
 $V = 1689.0$ (5) Å³
 $Z = 4$
 $D_x = 1.555$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 25 reflections
 $\theta = 7.3$ – 16.1°
 $\mu = 0.84$ mm⁻¹
 $T = 298$ (3) K
 Long parallelepiped
 $0.50 \times 0.31 \times 0.25$ mm
 Dark red

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
 $T_{\min} = 0.912$, $T_{\max} = 0.999$
 4694 measured reflections
 2199 independent reflections

2045 observed reflections [$I > 2.5\sigma(I)$]
 $R_{\text{int}} = 0.012$
 $\theta_{\max} = 22.5^\circ$
 $h = -7 \rightarrow 7$
 $k = 0 \rightarrow 19$
 $l = 0 \rightarrow 13$
 3 standard reflections
 frequency: 60 min
 intensity decay: 1.5%

Refinement

Refinement on F
 $R = 0.032$
 $wR = 0.051$
 $S = 2.02$
 2045 reflections
 225 parameters
 Only H-atom U 's refined
 Unit weights applied
 $(\Delta/\sigma)_{\max} = 0.02$

$\Delta\rho_{\max} = 0.52$ e Å⁻³
 $\Delta\rho_{\min} = -0.63$ e Å⁻³
 Extinction correction: secondary
 Extinction coefficient: 0.195 (18)
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Tc	0.50077 (8)	0.59648 (3)	0.22510 (5)	2.96 (3)
O1	0.2250 (7)	0.4917 (3)	0.1303 (4)	4.3 (2)
O2	0.3796 (8)	0.4445 (3)	0.2890 (5)	5.6 (3)
O3	0.3750 (7)	0.6509 (3)	0.3006 (4)	4.3 (2)

N1	0.3395 (8)	0.5473 (3)	0.1086 (5)	3.5 (3)
N2	0.5122 (8)	0.4933 (4)	0.2972 (5)	4.3 (3)
N3	0.5748 (8)	0.6454 (3)	0.0969 (5)	3.4 (3)
N4	0.7448 (8)	0.5933 (3)	0.2768 (5)	3.4 (3)
C1	0.3367 (9)	0.5765 (4)	0.0144 (6)	3.4 (3)
C2	0.6530 (11)	0.4792 (5)	0.3552 (6)	4.5 (4)
C3	0.4677 (10)	0.6365 (4)	-0.0017 (6)	3.5 (3)
C4	0.7927 (10)	0.5344 (5)	0.3554 (6)	4.4 (4)
C5	0.2096 (11)	0.5487 (6)	-0.0712 (7)	5.2 (5)
C6	0.6754 (13)	0.4069 (6)	0.4134 (9)	6.3 (5)
C7	0.3715 (13)	0.7070 (5)	-0.0354 (8)	5.3 (4)
C10	0.8162 (15)	0.5732 (7)	0.4687 (7)	6.9 (6)
C11	0.7413 (11)	0.6850 (5)	0.0792 (7)	4.6 (4)
C12	0.8977 (10)	0.6356 (5)	0.2408 (7)	4.4 (4)
C13	0.8403 (10)	0.7041 (5)	0.1821 (7)	4.1 (4)
C14	0.9989 (12)	0.7578 (5)	0.1671 (9)	5.6 (5)
C15	0.7507 (12)	0.7614 (5)	0.2547 (8)	5.0 (4)
C16	0.9218 (14)	0.8081 (7)	0.2519 (12)	8.1 (7)

Table 2. Selected geometric parameters (Å, °)

Tc—O3	1.664 (5)	C1—C3	1.479 (11)
Tc—N1	2.075 (6)	C1—C5	1.504 (10)
Tc—N2	2.087 (7)	C2—C4	1.446 (13)
Tc—N3	1.917 (6)	C2—C6	1.512 (12)
Tc—N4	1.917 (6)	C3—C7	1.528 (11)
O1—N1	1.353 (8)	C4—C10	1.588 (13)
O2—N2	1.330 (9)	C11—C13	1.511 (12)
N1—C1	1.290 (10)	C12—C13	1.507 (12)
N2—C2	1.290 (10)	C13—C14	1.545 (12)
N3—C3	1.465 (9)	C13—C15	1.539 (12)
N3—C11	1.452 (10)	C14—C16	1.518 (16)
N4—C4	1.493 (10)	C15—C16	1.531 (14)
N4—C12	1.449 (10)		
O3—Tc—N1	109.4 (2)	N1—C1—C3	115.2 (6)
O3—Tc—N2	108.3 (3)	C3—C1—C5	124.1 (7)
O3—Tc—N3	111.3 (3)	N2—C2—C4	116.0 (7)
O3—Tc—N4	111.3 (3)	N2—C2—C6	121.8 (8)
N1—Tc—N2	86.1 (3)	C4—C2—C6	122.1 (7)
N1—Tc—N3	77.7 (2)	N3—C3—C1	108.6 (6)
N1—Tc—N4	139.2 (2)	N3—C3—C7	112.6 (7)
N2—Tc—N3	140.2 (3)	C1—C3—C7	110.7 (6)
N2—Tc—N4	78.2 (3)	N4—C4—C2	109.6 (6)
N3—Tc—N4	90.8 (3)	N4—C4—C10	106.6 (7)
Tc—N1—O1	122.9 (4)	C2—C4—C10	112.4 (7)
Tc—N1—C1	117.5 (5)	N3—C11—C13	113.1 (7)
O1—N1—C1	119.2 (6)	N4—C12—C13	112.0 (6)
Tc—N2—O2	123.0 (5)	C11—C13—C12	110.7 (7)
Tc—N2—C2	116.7 (6)	C11—C13—C14	113.9 (7)
O2—N2—C2	120.2 (7)	C11—C13—C15	116.5 (7)
Tc—N3—C3	119.3 (5)	C12—C13—C14	111.9 (7)
Tc—N3—C11	127.8 (5)	C12—C13—C15	113.5 (7)
C3—N3—C11	112.5 (6)	C14—C13—C15	88.7 (6)
Tc—N4—C4	117.3 (5)	C13—C14—C16	90.2 (7)
Tc—N4—C12	128.4 (5)	C13—C15—C16	89.9 (7)
C4—N4—C12	113.9 (6)	C14—C16—C15	90.0 (7)
N1—C1—C5	120.7 (7)		

The structure was solved by Patterson methods and Fourier synthesis, and refined by full-matrix least squares. H atoms were located by a difference Fourier method and refined isotropically.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*. Program(s) used to refine structure: *NRCVAX*. Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1986). Software used to prepare material for publication: *NRCVAX*.

The authors thank the National Science Council for support under grants NSC 84-2112-M007-019 and NSC 84-2113-M007-027. They are also indebted to Ms Shu-Fang Tung for collecting the X-ray diffraction data.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: KH1061). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 840–842

[Fe₂(CO)₄(PMe₃)₄(μ-H)(μ-SiCl₂)]- [Fe(CO)₄(SiCl₃)]

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(Received 10 November 1994; accepted 9 October 1995)

Abstract

The structure of tetracarbonyl-μ-(dichlorosilylene)-μ-hydrido-tetrakis(trimethylphosphine)diiron(1+) tetracarbonyl(trichlorosilyl)ferrate(1-), has been determined at 119 K. The cation has an Fe—Fe distance of 2.947(2) Å and an average Fe—Si distance of