scan time ratio of 0.5. The Bijvoet mate was measured for every 15th reflection throughout the intensity-data collection. No decay correction was applied but the data were corrected for Lorentz and polarization effects and for absorption; ψ-scan absorption data were taken at the end of data collection, the correction method being that of North, Phillips & Mathews (1968). Systematic absences (hkl, $h + k$ = odd) were consistent with three space groups: $C2$, Cm and $C2/m$. Solutions were attempted in each. For the two non-centrosymmetric space groups, $C2$ and Cm, solutions exhibited high correlation coeffients and non-positive-definite displacement parameters, while refinement proceeded well for the centrosymmetric space group, $C2/m$ (No. 12); the latter was adopted. The direct-methods program *SHELXS*86 (Sheldrick, 1985) produced an E map from which the initial positions of the Ca cation and the C and O atoms of the organic anion were determined. The positions of the water O atoms and the H atoms were subsequently identified using difference Fourier methods. The water molecule O(3) atom was found at a general position and refined normally. The water molecule O(4) atom was found at a $2/m$ site $(0,\frac{1}{2},0)$ and refined with B_{eq} = 13.5 Å^2, indicating disorder. The disorder was then modeled by placing O(4) slightly off the twofold axis but still on the mirror. This model refined to give the smaller B_{eq} values listed in Table 1, and also a lower R value. [The disorder of O(4) was also present in the structures determined in $C2$ and Cm.] The Ca, O and C atoms were refined anisotropically and the ring H atoms refined isotropically using full-matrix least squares (*TEXSAN*; Molecular Structure Corporation, 1989). Following convergence, three of the top four peaks in the difference map were within 1.0 Å of O(3) which suggested further disorder, possibly due to the disorder of O(4). Two H atoms were distributed over these three sites using occupancy factors determined from the relative peak heights on the difference map. These partial-occupancy H atoms, with fixed positional and displacement parameters, were included in the final refinement cycles. The maximum peak on the final electron density difference map was located near (0,0,0), approximately at the midpoint of the central bond of the naphthalene ring. The minimum peak was located near (0.55,0.20,0.16), approximately 1.2 Å from O(3) and 2.1 Å from Ca.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, least-squares-planes data and hydrogen-bond geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71405 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1060]

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trans-Bisaquabis[1,2-bis(diphenylphosphino)-ethane]technetium(I) Tetraphenylborate

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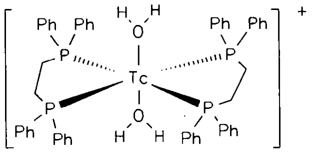
Abstract

The title compound, *trans*-bisaquabis[1,2-ethanediylbis(diphenylphosphine)]technetium tetraphenylborate, $[Tc(C_{26}H_{24}P_2)_2(H_2O)_2][B(C_6H_5)_4]$, consists of packed $[Tc(H_2O)_2(dppe)_2]^+$ cations [dppe is 1,2-bis(diphenylphosphino)ethane] and tetraphenylborate anions. The Tc atom is coordinated in an octahedral environment. The two aqua ligands are in a *trans* arrangement with Tc—O distances of 2.307 (4) and 2.252 (4) Å and an O1—Tc—O2 angle of 175.7 (2)°. The equatorial Tc—P distances fall in the range 2.493 (2)–2.505 (2) Å.

Comment

Technetium complexes are widely used in diagnostic nuclear medicine (Clarke & Podbielski, 1987) and because of this there is considerable interest in the chemistry of this artificial element, especially in the development of new organ-specific agents where exact knowledge of the chemical and structural properties of technetium complexes is required.

Cationic Tc complexes with chelating phosphines have been discussed as potential tracers for cardiac scintigraphy (Deutsch, Libson, Jurisson & Lindoy, 1983). Some of these compounds have been structurally characterized (Melnik & van Lier, 1987; Konno, Heeg & Deutsch, 1988; Archer, Dilworth, Griffiths, McPartlin & Kelly, 1992). In this context, as part of our systematic studies on technetium compounds, the crystal structure of $[Tc(H_2O)_2(dppe)_2](BPh_4)$ (I) was determined (BPh_4 = tetraphenylborate). The compound was isolated as a by-product during the synthesis of $[TcN(Cl)(dppe)_2](BPh_4)$ by the reaction of $[TcNCl_2(Ph_3P)_2]$ with excess dppe. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a CH_2Cl_2/isopropanol solution.



(I)

The metal in the title compound is coordinated in a distorted octahedral environment. A *SCHAKAL* plot (Keller, 1989) of the cation is shown in Fig. 1. Two H_2O ligands occupy the axial positions with a mean Tc—O bond length of 2.28 Å. This value is shorter than that found in compounds with aqua ligands in positions *trans* to Tc═O (Mantegazzi, Ianoz, Lerch & Tatsumi, 1990) and Tc≡N bonds (Baldas, Colmanet & Williams, 1991; Baldas, Boas, Colmanet & Mackay, 1990) due to the *trans*-labilizing effect of the O^{2-} and N^{3-} ligands in the latter complexes. The Tc—P bond lengths are in the range typical of Tc complexes with the metal in low oxidation states (Melnik & van Lier, 1987).

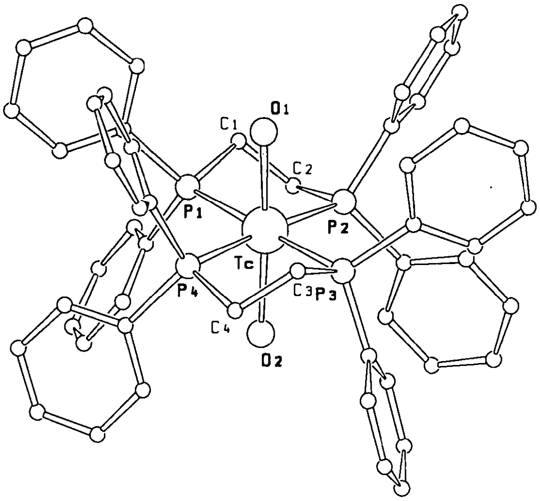


Fig. 1. *SCHAKAL* plot of $[Tc(H_2O)_2(dppe)_2]^+$ showing the atomic numbering scheme.

A nearly linear arrangement is found for the two axial O donors. The P atoms are bent out of the equatorial plane by 0.048 (2) Å. This, however, can be understood with regard to the steric requirement of the bulky phenyl groups.

Experimental

Crystal data

$[Tc(C_{26}H_{24}P_2)_2(H_2O)_2]$-
$[B(C_6H_5)_4]$
M_r = 1250.13
Monoclinic
$P2_1/c$
a = 10.342 (2) Å
b = 24.358 (2) Å
c = 25.962 (5) Å
β = 96.358 (9)°
V = 6499 (2) Å^3
Z = 4

D_x = 1.277 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.54056 Å
Cell parameters from 24 reflections
θ = 5-69°
μ = 3.11 mm^{-1}
T = 295 K
Block
0.4 × 0.2 × 0.2 mm
Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
T_{min} = 0.65, T_{max} = 1.50
13 075 measured reflections
12 757 independent reflections
6522 observed reflections $[I \geq 3\sigma(I)]$

R_{int} = 0.028
θ_{max} = 69°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 29$
$l = -31 \rightarrow 31$
3 standard reflections monitored every 200 reflections
intensity variation: 27.8% (0.24% h^{-1})

Refinement

Refinement on F^2
R = 0.068
wR = 0.073
S = 3.943
6522 reflections
758 parameters
H-atom parameters not refined
$w = 1/\sigma^2$
$(\Delta/\sigma)_{max}$ = 0.01

$\Delta\rho_{max}$ = 0.901 e Å^{-3}
$\Delta\rho_{min}$ = 0.247 e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: 2.363 × 10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Programs used: *SHELXS*86 (Sheldrick, 1986), *MolEN* (Fair, 1990), *SDP* (Frenz, 1986). Computer used: DEC VAX Station 3100.

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

$$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Tc	0.10880 (7)	0.47023 (3)	0.24626 (3)	4.42 (1)
P1	0.2108 (2)	0.56364 (9)	0.24933 (9)	4.61 (5)
P2	0.1124 (2)	0.4880 (1)	0.34133 (9)	4.68 (5)
P3	0.0033 (2)	0.37791 (9)	0.24308 (9)	4.49 (5)
P4	0.1161 (3)	0.4481 (1)	0.15288 (9)	5.44 (6)
O1	−0.0855 (4)	0.5091 (2)	0.2212 (2)	4.7 (1)
O2	0.3096 (4)	0.4295 (2)	0.2655 (2)	2.63 (8)
C1	0.1735 (9)	0.5911 (4)	0.3112 (4)	6.0 (2)
C2	0.216 (1)	0.5489 (4)	0.3528 (3)	6.2 (2)
C3	−0.0529 (9)	0.3670 (4)	0.1751 (4)	5.8 (2)
C4	0.068 (1)	0.3767 (4)	0.1448 (4)	6.8 (3)
C11	0.1560 (9)	0.6171 (4)	0.2017 (4)	5.6 (2)
C12	0.035 (1)	0.6400 (5)	0.2008 (5)	7.9 (3)
C13	−0.008 (1)	0.6784 (5)	0.1621 (5)	9.6 (4)
C14	0.071 (2)	0.6918 (5)	0.1250 (5)	10.6 (4)
C15	0.189 (1)	0.6681 (6)	0.1255 (5)	10.7 (4)
C16	0.233 (1)	0.6320 (5)	0.1639 (4)	8.2 (3)
C21	0.3843 (8)	0.5698 (3)	0.2531 (4)	5.3 (2)
C22	0.4538 (9)	0.5355 (4)	0.2234 (4)	6.4 (2)
C23	0.589 (1)	0.5443 (4)	0.2216 (5)	7.7 (3)
C24	0.6500 (9)	0.5850 (4)	0.2515 (5)	8.1 (3)
C25	0.582 (1)	0.6178 (4)	0.2828 (5)	8.7 (3)
C26	0.4505 (9)	0.6106 (4)	0.2824 (4)	6.8 (3)
C31	−0.0312 (9)	0.5110 (4)	0.3698 (4)	6.3 (2)
C32	−0.152 (1)	0.5032 (6)	0.3462 (4)	9.0 (3)
C33	−0.258 (1)	0.5228 (8)	0.3699 (5)	15.3 (5)
C34	−0.241 (1)	0.5491 (6)	0.4139 (5)	14.8 (4)
C35	−0.121 (2)	0.5552 (6)	0.4385 (5)	14.6 (4)
C36	−0.018 (1)	0.5368 (6)	0.4170 (5)	10.6 (3)
C41	0.1783 (8)	0.4354 (4)	0.3869 (3)	5.0 (2)
C42	0.096 (1)	0.4008 (4)	0.4100 (4)	6.2 (2)
C43	0.144 (1)	0.3595 (5)	0.4421 (4)	8.1 (3)
C44	0.275 (1)	0.3509 (5)	0.4514 (4)	8.9 (3)
C45	0.361 (1)	0.3844 (5)	0.4290 (4)	7.8 (3)
C46	0.313 (1)	0.4274 (4)	0.3962 (4)	6.3 (3)
C51	−0.1387 (8)	0.3676 (4)	0.2757 (4)	5.2 (2)
C52	−0.2526 (9)	0.3935 (5)	0.2575 (5)	8.9 (3)
C53	−0.3631 (9)	0.3879 (6)	0.2836 (6)	10.8 (4)
C54	−0.360 (1)	0.3555 (6)	0.3254 (5)	10.4 (4)
C55	−0.250 (1)	0.3279 (6)	0.3434 (5)	9.3 (4)
C56	−0.1406 (9)	0.3332 (5)	0.3177 (4)	6.7 (3)
C61	0.1082 (8)	0.3196 (3)	0.2591 (3)	4.8 (2)
C62	0.200 (1)	0.3213 (4)	0.3027 (4)	6.3 (2)
C63	0.285 (1)	0.2785 (4)	0.3143 (5)	7.5 (3)
C64	0.284 (1)	0.2334 (5)	0.2831 (5)	7.6 (3)
C65	0.196 (1)	0.2301 (4)	0.2409 (4)	7.1 (3)
C66	0.107 (1)	0.2726 (4)	0.2286 (4)	6.3 (2)
C71	0.276 (1)	0.4499 (4)	0.1275 (3)	5.8 (2)
C72	0.309 (1)	0.4937 (5)	0.1002 (4)	9.6 (4)
C73	0.433 (1)	0.4976 (6)	0.0839 (5)	11.9 (4)
C74	0.516 (1)	0.4563 (6)	0.0976 (5)	12.5 (4)
C75	0.487 (1)	0.4115 (6)	0.1258 (6)	11.5 (4)
C76	0.363 (1)	0.4088 (5)	0.1416 (4)	8.5 (3)
C81	−0.000 (1)	0.4825 (5)	0.1054 (4)	7.1 (3)
C82	−0.062 (1)	0.4581 (6)	0.0642 (4)	10.3 (4)
C83	−0.150 (1)	0.4834 (7)	0.0296 (5)	12.4 (5)
C84	−0.182 (1)	0.5346 (6)	0.0356 (5)	11.1 (4)
C85	−0.128 (2)	0.5602 (7)	0.0760 (6)	20.0 (6)
C86	−0.032 (2)	0.5339 (6)	0.1117 (6)	20.1 (6)
C91	0.121 (1)	0.7565 (4)	0.9502 (4)	6.7 (3)
C92	0.069 (1)	0.7126 (5)	0.9760 (4)	8.7 (3)
C93	−0.065 (1)	0.7041 (6)	0.9760 (5)	11.2 (4)
C94	−0.149 (1)	0.7383 (7)	0.9491 (5)	12.4 (5)
C95	−0.110 (1)	0.7822 (6)	0.9233 (6)	11.1 (4)
C96	0.027 (1)	0.7900 (5)	0.9251 (5)	8.7 (3)
C101	0.3023 (9)	0.8338 (4)	0.9674 (4)	5.7 (2)
C102	0.3943 (9)	0.8687 (4)	0.9476 (4)	6.2 (2)
C103	0.416 (1)	0.9227 (4)	0.9625 (4)	6.9 (3)
C104	0.344 (1)	0.9450 (5)	0.9985 (5)	7.5 (3)
C105	0.253 (1)	0.9138 (5)	1.0193 (5)	8.3 (3)
C106	0.234 (1)	0.8597 (4)	1.0038 (5)	8.0 (3)
C111	0.362 (1)	0.7294 (4)	0.9921 (4)	7.1 (3)
C112	0.381 (2)	0.6737 (5)	0.9819 (5)	11.8 (5)
C113	0.450 (2)	0.6390 (6)	1.0149 (5)	14.3 (5)
C114	0.508 (2)	0.6570 (6)	1.0606 (6)	13.7 (5)
C115	0.492 (2)	0.7104 (6)	1.0736 (6)	12.9 (5)
C116	0.419 (1)	0.7450 (5)	1.0393 (5)	8.8 (3)
C121	0.328 (1)	0.7593 (4)	0.8928 (4)	6.4 (3)
C122	0.245 (1)	0.7608 (4)	0.8455 (4)	7.5 (3)
C123	0.291 (1)	0.7528 (5)	0.7990 (4)	9.4 (3)
C124	0.419 (1)	0.7442 (5)	0.7951 (4)	11.8 (4)
C125	0.505 (1)	0.7423 (5)	0.8396 (5)	11.1 (4)
C126	0.456 (1)	0.7501 (5)	0.8874 (5)	8.9 (3)
B	0.278 (1)	0.7698 (5)	0.9512 (4)	5.9 (3)

Table 2. *Selected geometric parameters* (Å, °)

Tc—O1	2.252 (4)	Tc—P2	2.502 (2)
Tc—O2	2.307 (4)	Tc—P3	2.498 (2)
Tc—P1	2.505 (2)	Tc—P4	2.493 (2)
O1—Tc—O2	175.7 (2)	O2—Tc—P3	90.0 (1)
O1—Tc—P1	89.2 (1)	O2—Tc—P4	89.7 (1)
O1—Tc—P2	97.4 (1)	P1—Tc—P2	81.4 (1)
O1—Tc—P3	89.8 (1)	P1—Tc—P3	179.0 (1)
O1—Tc—P4	86.1 (1)	P2—Tc—P3	98.5 (1)
O2—Tc—P1	91.0 (1)	P2—Tc—P4	176.4 (1)
O2—Tc—P2	86.9 (1)	P3—Tc—P4	80.4 (1)

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Lists of structure factors, anisotropic displacement parameters (*U* and *B*), H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71451 (46 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1056]

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