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Hexacarbonyltechnetium(I) perchlorate

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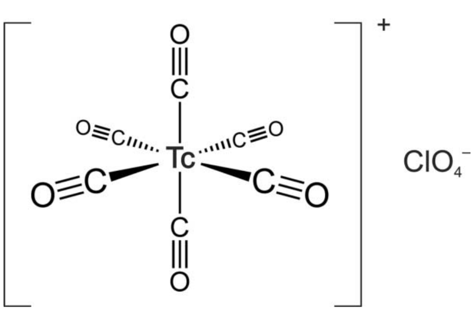
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(O–C) = 0.004 Å; disorder in main residue; R factor = 0.031; wR factor = 0.068; data-to-parameter ratio = 15.2.

The title compound, $[Tc(CO)_6]ClO_4$, was synthesized by the reaction of $[TcCl(CO)_5]$ with $AgClO_4$, followed by acidification with $HClO_4$ under a CO atmosphere. The $[Tc(CO)_6]^+$ cation has close to idealized octahedral geometry, with the bond angles between *cis*-CO groups close to 90° and the Tc—C bond lengths in the range 2.025 (3)–2.029 (3) Å. The perchlorate anion is disordered over two crystallographically equivalent half-occupied positions. The Tc atom in the $[Tc(CO)_6]^+$ cation is located on an inversion centre.

Related literature

For the first report on the $[Tc(CO)_6]^+$ cation, see: Hieber *et al.* (1965). For related literature, see: Aebischer *et al.* (2000); Alberto *et al.* (1996, 1998); Baturin *et al.* (1994*a*,*b*); Grigor'ev *et al.* (1997*a*,*b*); Miroslavov *et al.* (2008*a*,*b*); Schwochau (2000).



Experimental

Crystal data

$[Tc(CO)_6]ClO_4$
M_r = 366.42
Monoclinic, $C2/c$
a = 13.227 (4) Å
b = 6.8002 (18) Å
c = 13.616 (3) Å
β = 112.56 (2)°
V = 1131.0 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.55 mm^{-1}
T = 293 (2) K
0.20 × 0.18 × 0.10 mm

Data collection

Stoe IPDS-2 diffractometer
Absorption correction: integration (*X-RED* and *X-SHAPE*; Stoe & Cie, 2005)
T_{min} = 0.620, T_{max} = 0.723
4935 measured reflections
1508 independent reflections
1224 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.067
S = 1.06
1508 reflections
99 parameters
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Data collection: *X-AREA* (Stoe & Cie, 2007); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2005); program(s) used to solve structure: *SHELXL97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *publCIF* (Westrip, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2134).

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supplementary materials

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Hexacarbonyltechnetium(I) perchlorate

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Comment

Among technetium(I) carbonyl complexes, the highest carbonyl, $[Tc(CO)_6]^+$ cation, is the least studied compared to penta-, tetra-, and especially tricarbonyl complexes (Schwochau, 2000). No data on the crystal structure of its salts are available. More detailed study of this cation is significant for the development of the coordination chemistry of technetium (and d block as a whole). The first report on the $[Tc(CO)_6]^+$ cation is dated by Hieber *et al., 1965* prepared this species in the form of the solid compound $[Tc(CO)_6][AlCl_4]$ by the solid-phase reaction of $[TcCl(CO)_5]$ with $AlCl_3$ under high CO pressure (300 atm) at 363 K (Heiber *et al.*, 1965). The product was characterized by chemical analysis, and the cation appeared to be stable in solutions. Relatively recently (Aebischer *et al.*, 2000) observed successive formation of higher technetium carbonyls $[Tc(CO)_n(H_2O)_{6–n}]^+$ (n = 4–6) in aqueous solution (2 *M* $HClO_4$) from the complex $[Tc(CO)_3(H_2O)_3]^+$ at room temperature and moderately high CO pressure (about 50 atm), after removal of chloride ions. The reaction progress was monitored by the ^{99}Tc and ^{13}C NMR. The relative content of the $[Tc(CO)_6]^+$ cation in the mixture of technetium carbonyl species was low, and no solid salt of this cation was isolated. Here we report on the synthesis and crystal structure of hexacarbonyltechnetium(I) perchlorate, $[Tc(CO)_6]ClO_4$.

Experimental

Pentacarbonyltechnetium chloride $[TcCl(CO)_5]$ (SU Inventor's Certificate 1512003) was dissolved in boiled water, and a stoichiometric amount of $AgClO_4$ was added after cooling to remove chloride ions interfering with the synthesis (Miroslavov *et al.*, 2008*a*). The resulting solution was acidified with $HClO_4$ to a concentration of 2 *M* and treated with CO in a pressure vessel (443 K, 150 atm, 1 h). After completing the reaction and removing the excess of CO, the reaction system consisted of an aqueous solution and a colorless crystalline precipitate. The precipitate was separated, washed with water and methylene chloride (to remove an impurity of $[TcCl(CO)_5]$ (Miroslavov *et al.*, 2008*a*)), and dried in air. The product was identified as $[Tc(CO)_6]ClO_4$. Some of the crystals appeared to be suitable for an X-ray diffraction analysis. ^{99}Tc NMR(CH_3OH): -1924 p.p.m.. IR (CH_3CN): n_{CO} 2095 cm^{-1}. Found Tc, %: 27.12. $C_6ClO_{10}Tc$. Calculated Tc, %: 27.01. The IR spectrum was recorded on a Shimadzu FTIR 8700 spectrophotometer. The ^{99}Tc NMR spectrum was taken on a Bruker WP-200 spectrometer.

Refinement

The crystal structure of $[Tc(CO)_6]ClO_4$ contains one symmetrically independent Tc^+ cation octahedrally coordinated by six carbon atoms (Figs. 1, 2). The Tc—C=O fragments are linear to within 3°. The coordination polyhedron of technetium in the $[Tc(CO)_6]^+$ cation is close to an ideal octahedron, with the bond angles between *cis*-CO groups equal to 90° (within

±1.5°) and the Tc–C bond lengths in the range of 2.025–2.029 Å. These distances are significantly (by 0.1–0.15 Å) longer than the Tc–C distances in *trans*-OC–Tc–σ donor fragments, *e.g.*: $[TcI(CO)_5]$($Tc–C_{trans\text{-}I}$) 1.938 (Grigor'ev *et al.*, 1997*a*), $[TcI(CO)_4]_2$ ($Tc–C_{trans\text{-}I}$) 1.89–1.92 (Grigor'ev *et al.*, 1997*b*), $[TcCl(CO)_3]_4$ 1.903 (Baturin *et al.*, 1994*a*), $[TcBr(CO)_3(en)]$ 1.882–1.889 (Baturin *et al.*, 1994*b*), $[Tc(OH)(CO)_3]_4$ 1.886–1.905 Å (Alberto *et al.*, 1998). At the same time, they are only slightly longer than the Tc–C distances in *trans*-OC–Tc–π acceptor fragments of other structurally examined complexes (π acceptor is another CO group, PPh_3, or Bu^tNC): $[Tc(CO)_5(Bu^tNC)]ClO_4$ 1.999–2.022 (Miroslavov *et al.*, 2008*b*), $[Tc(CO)_5(PPh_3)]CF_3SO_3$ 1.985–2.019 (Alberto *et al.*, 1998) (in these two compounds, the lengths of the equatorial and axial Tc–CO bonds are similar), [*fac*-$Tc(CO)_3(Bu^tNC)_3]NO_3$ 1.963–1.975 (Alberto *et al.*, 1996) $[TcI(CO)_5]$ (Tc–C~trans-CO~) 2.015 (Grigor'ev *et al.*, 1997*a*), $[TcI(CO)_4]_2$ ($Tc–C_{trans\text{-}CO}$) 1.98–2.01 Å (Grigor'ev *et al.*, 1997*b*). The large difference between the Tc–CO bond lengths in cases when the transposition to the CO group is occupied by a π acceptor or a σ donor can be attributed to the *trans* effect (competition between the π acceptors arranged *trans* to each other for the same occupied d orbital of the metal ion). A certain *cis* effect, however, also takes place, because the Tc–CO bonds in the $[Tc(CO)_6]^+$ cation are somewhat longer than the Tc–CO bonds in *trans*-OC–Tc–CO fragments of complexes containing in *cis* positions ligands that are σ donors or π acceptors weaker than CO.

The Cl atom in the structure of $[Tc(CO)_6]ClO_4$ is tetrahedrally coordinated by four O atoms (mean Cl–O distance is 1.403 Å). The perchlorate anion is disordered over two crystallographically equivalent half-occupied positions (Fig. 2) with the total site-occupation factor (s.o.f.) equal to 1.0. The central atoms of $[Tc(CO)_6]^+$ octahedra and $[ClO_4]^-$ tetrahedra (Tc and Cl respectively) form a distorted NaCl-type lattice oriented along a_{NaCl} [110], b_{NaCl} [10–1], c_{NaCl} [-110] (Fig. 3).

Figures

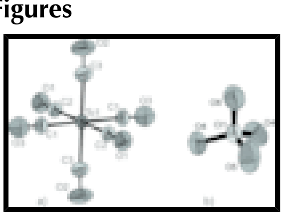

Fig. 1. View of the $[Tc(CO)_6]^+$cation (*a*) and one component of the disordered perchlorate anion (*b*) in the structure of $[Tc(CO)_6]ClO_4$. Thermal ellipsoids are drawn at the 50% probability level.

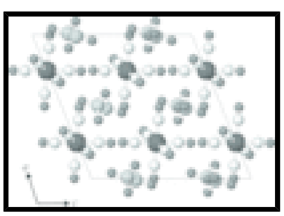

Fig. 2. Crystal structure of $[Tc(CO)_6]ClO_4$. Tc atoms are dark-grey, O atoms are grey, Cl atoms are light-grey, and C atoms are white circles.

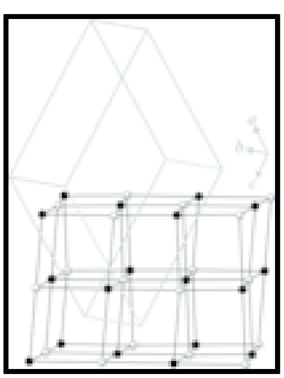

Fig. 3. Relationship of title structure to NaCl structure.

Hexacarbonyltechnetium(I) perchlorate

Crystal data

$[Tc(CO)_6]ClO_4$	$F_{000} = 704$
$M_r = 366.42$	$D_x = 2.152$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 5446 reflections
$a = 13.227$ (4) Å	$\theta = 2.0$–29.6°
$b = 6.8002$ (18) Å	$\mu = 1.55$ mm^{-1}
$c = 13.616$ (3) Å	$T = 293$ (2) K
$\beta = 112.56$ (2)°	Prism, colorless
$V = 1131.0$ (5) Å^3	0.20 × 0.18 × 0.10 mm
$Z = 4$	

Data collection

Stoe IPDS-2 diffractometer	1508 independent reflections
Radiation source: fine-focus sealed tube	1224 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.035$
Detector resolution: 6.67 pixels mm^{-1}	$\theta_{max} = 29.2$°
$T = 293(2)$ K	$\theta_{min} = 3.2$°
rotation method scans	$h = -18 \rightarrow 18$
Absorption correction: integration (X-RED and X-SHAPE; Stoe & Cie, 2005)	$k = -9 \rightarrow 8$
$T_{min} = 0.620$, $T_{max} = 0.723$	$l = -18 \rightarrow 18$
4935 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0289P)^2 + 1.543P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.031$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.067$	$\Delta\rho_{max} = 0.32$ e Å^{-3}
$S = 1.06$	$\Delta\rho_{min} = -0.44$ e Å^{-3}
1508 reflections	Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
99 parameters	Extinction coefficient: 0.0043 (12)
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Tc1	0.2500	0.2500	0.0000	0.03673 (14)	
C1	0.2509 (2)	0.1350 (5)	0.1375 (2)	0.0484 (7)	
C2	0.3021 (2)	−0.0119 (5)	−0.0345 (2)	0.0446 (6)	
C3	0.4088 (2)	0.3328 (5)	0.0721 (3)	0.0501 (7)	
O1	0.3312 (2)	−0.1557 (4)	−0.0529 (2)	0.0632 (6)	
O2	0.49658 (19)	0.3762 (4)	0.1078 (3)	0.0774 (8)	
O3	0.2481 (2)	0.0685 (5)	0.2111 (2)	0.0778 (8)	
O4	0.0932 (2)	−0.2268 (5)	−0.1933 (3)	0.0814 (9)	
O5	0.503 (3)	0.0179 (9)	0.2724 (16)	0.109 (7)	0.50
O6	0.5401 (5)	−0.1423 (12)	0.1398 (5)	0.0856 (18)	0.50
Cl1	0.50996 (15)	−0.1697 (2)	0.22853 (14)	0.0480 (4)	0.50

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tc1	0.03421 (17)	0.04318 (19)	0.03316 (17)	0.00255 (14)	0.01331 (11)	−0.00340 (15)
C1	0.0481 (15)	0.0592 (18)	0.0423 (16)	0.0126 (13)	0.0222 (12)	0.0041 (13)
C2	0.0403 (13)	0.0519 (15)	0.0404 (14)	0.0037 (12)	0.0141 (11)	−0.0028 (12)
C3	0.0418 (14)	0.0527 (15)	0.0545 (18)	0.0005 (13)	0.0172 (13)	−0.0074 (14)
O1	0.0693 (15)	0.0567 (14)	0.0658 (16)	0.0148 (12)	0.0284 (12)	−0.0076 (12)
O2	0.0433 (12)	0.0782 (18)	0.105 (2)	−0.0091 (12)	0.0216 (13)	−0.0225 (16)
O3	0.0830 (18)	0.105 (2)	0.0609 (16)	0.0297 (16)	0.0444 (14)	0.0249 (16)
O4	0.0566 (14)	0.096 (2)	0.087 (2)	−0.0202 (14)	0.0229 (14)	−0.0261 (16)
O5	0.077 (4)	0.074 (3)	0.155 (19)	−0.002 (8)	0.021 (12)	−0.052 (8)
O6	0.072 (3)	0.120 (5)	0.061 (3)	−0.019 (3)	0.021 (3)	0.019 (4)
Cl1	0.0366 (7)	0.0512 (6)	0.0497 (12)	−0.0023 (6)	0.0094 (6)	−0.0015 (6)

Geometric parameters (Å, °)

Tc1—C1^{i}	2.025 (3)	O5—O5^{iv}	0.59 (4)
Tc1—C1	2.025 (3)	O5—Cl1^{iv}	1.286 (8)
Tc1—C3^{i}	2.027 (3)	O5—Cl1	1.428 (11)

Tc1—C3	2.027 (3)	O6—Cl1	1.422 (6)
Tc1—C2^{i}	2.029 (3)	O6—Cl1^{iv}	2.144 (6)
Tc1—C2	2.029 (3)	Cl1—Cl1^{iv}	0.728 (3)
C1—O3	1.113 (4)	Cl1—O5^{iv}	1.286 (8)
C2—O1	1.114 (4)	Cl1—O4^{v}	1.393 (3)
C3—O2	1.113 (4)	Cl1—O4^{iii}	1.444 (3)
O4—Cl1^{ii}	1.393 (3)	Cl1—O6^{iv}	2.144 (6)
O4—Cl1^{iii}	1.444 (3)		
C1^{i}—Tc1—C1	180.0 (2)	O1—C2—Tc1	179.6 (3)
C1^{i}—Tc1—C3^{i}	91.27 (14)	O2—C3—Tc1	177.0 (3)
C1—Tc1—C3^{i}	88.73 (14)	O5^{iv}—Cl1—O4^{v}	124.7 (11)
C1^{i}—Tc1—C3	88.73 (14)	O4^{v}—Cl1—O5	107.0 (10)
C1—Tc1—C3	91.27 (14)	O5^{iv}—Cl1—O6	86.5 (11)
C3^{i}—Tc1—C3	180.0 (3)	O4^{v}—Cl1—O6	108.6 (3)
C1^{i}—Tc1—C2^{i}	89.61 (12)	O5—Cl1—O6	108.9 (9)
C1—Tc1—C2^{i}	90.39 (12)	O5^{iv}—Cl1—O4^{iii}	112.3 (14)
C3^{i}—Tc1—C2^{i}	88.56 (12)	O4^{v}—Cl1—O4^{iii}	112.1 (3)
C3—Tc1—C2^{i}	91.44 (12)	O5—Cl1—O4^{iii}	111.5 (13)
C1^{i}—Tc1—C2	90.39 (12)	O6—Cl1—O4^{iii}	108.6 (3)
C1—Tc1—C2	89.61 (12)	O5^{iv}—Cl1—O6^{iv}	80.9 (11)
C3^{i}—Tc1—C2	91.44 (12)	O4^{v}—Cl1—O6^{iv}	79.2 (2)
C3—Tc1—C2	88.56 (12)	O5—Cl1—O6^{iv}	58.6 (10)
C2^{i}—Tc1—C2	180.00 (17)	O6—Cl1—O6^{iv}	167.4 (6)
O3—C1—Tc1	177.6 (3)	O4^{iii}—Cl1—O6^{iv}	76.4 (2)

Symmetry codes: (i) $-x+1/2, -y+1/2, -z$; (ii) $x-1/2, -y-1/2, z-1/2$; (iii) $-x+1/2, -y-1/2, -z$; (iv) $-x+1, y, -z+1/2$; (v) $x+1/2, -y-1/2, z+1/2$.

Fig. 1

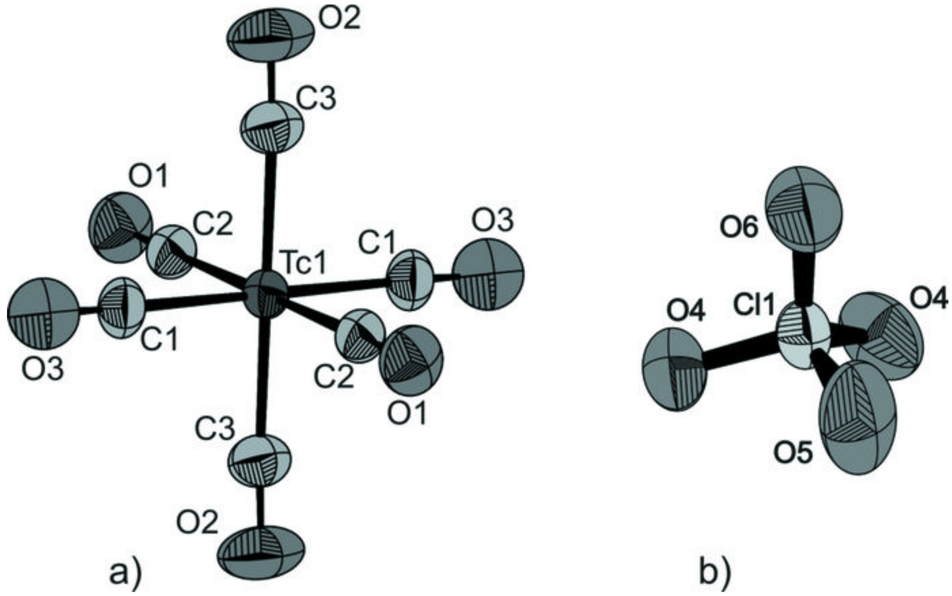

Fig. 2

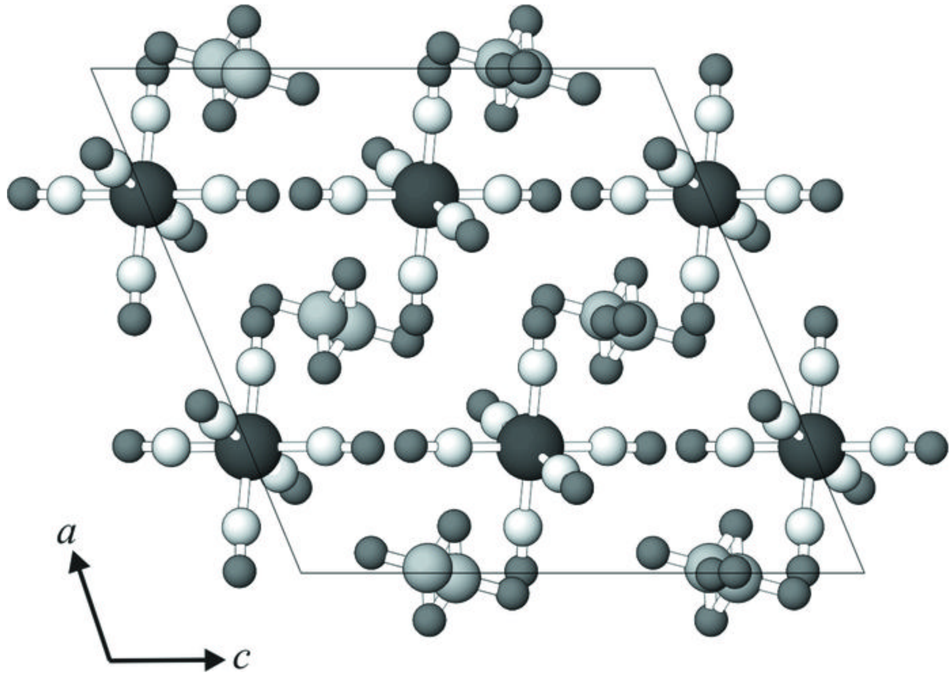

Fig. 3