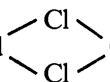


Cd—Cl distances fall into two categories; for Cl atoms which are shared between two Cd atoms Cd—Cl ranges from 2.535 (7) to 2.586 (7) Å and for those which are shared by three Cd atoms Cd—Cl ranges from 2.629 (7) to 2.759 (6) Å. Cd—O(water) is 2.50 (4) Å which is longer than the Cd—O(water) distances of 2.356 (4) Å found in Cd<sub>2</sub>NiCl<sub>6</sub>·12H<sub>2</sub>O (Leclaire & Borel, 1980*a*) and 2.328 (4) Å in Cd<sub>4</sub>NiCl<sub>10</sub>·10H<sub>2</sub>O (Leclaire & Borel, 1980*b*). There is no Cl—O(water) distance less than 3.5 Å so the water molecule is assumed not to form hydrogen bonds to Cl atoms. The (CdCl<sub>6</sub>) and [CdCl<sub>5</sub>(H<sub>2</sub>O)] octahedra are distorted so that all Cl—Cd—Cl

angles in Cd  Cd units are less than 90° [83.3 (2) to 86.8 (2)°].

The structure was solved and refined assuming the space group *Pnma* which implies that the crown is on a mirror plane. The unusual geometry of the crown, e.g. the abnormally short C(8)—C(8<sup>ii</sup>) distance, and especially the unusual torsion angles, notably all O—C—C—O being close to zero, suggest that the crown is disordered. This is also indicated by the large 'thermal' parameters. Attempts at untangling the disorder by replacing the anisotropic atoms by pairs of isotropic atoms and trying to fit two crowns to these new positions were unsuccessful. The 3:1 adduct of CdCl<sub>2</sub> with 15C5 exhibits a radiation-induced phase transition (Hazell, Hazell, Holm & Krogh, 1991) where the crown becomes disordered and the structure becomes centrosymmetric, a similar effect could occur in the 4:1 complex, which also suffers from radiation damage, but the change here from *Pn2<sub>1</sub>a* to *Pnma* would not be as easy to detect since the space-group absences would remain unchanged. Also there was no broadening of the peaks as was observed for the 3:1 adduct.

The O atoms of the crown ether are strongly bonded to Cd, the Cd—O distances range from 2.44 (2) to 2.53 (2) Å, which is longer than those in the 3:1 adduct of CdCl<sub>2</sub> and 15C5 [2.22 (2) to 2.38 (2) Å] where the cadmium is at the centre of the crown (Hazell, Hazell, Holm & Krogh, 1991) but considerably shorter than those in the 18-crown-6 compound (Paige & Richardson, 1984).

We are indebted to the Carlsberg Foundation and to the Danish Science Research Council for the diffractometer.

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## Structures of *trans*-[TcCl<sub>4</sub>{P(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}<sub>2</sub>], [TcCl<sub>4</sub>{P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>}<sub>2</sub>] and [P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>H][TcCl<sub>5</sub>{P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>}]

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**Abstract.** *trans*-Tetrachlorobis(methyldiphenylphosphine)technetium, (I), *M<sub>r</sub>* = 641.16, triclinic, *P* $\bar{1}$ , *a* =

8.991 (5), *b* = 9.603 (4), *c* = 9.750 (6) Å,  $\alpha$  = 66.67 (4),  $\beta$  = 88.65 (4),  $\gamma$  = 62.80 (4)°, *V* = 674.6 (6) Å<sup>3</sup>, *Z* = 1, *D<sub>x</sub>* = 1.573 Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha)$  = 0.71069 Å,  $\mu$  = 1.04 mm<sup>-1</sup>, *F*(000) = 323, *T* =

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295 K and  $R = 0.039$  for 2441 observed reflections. The Tc atom is located on an inversion centre. The Tc—P distances are 2.556 (1) Å while the Tc—Cl bonds are 2.324 (1) and 2.320 (1) Å. *trans*-Tetrachlorobis(triethylphosphine)technetium, (II),  $M_r = 447.04$ , monoclinic,  $P2_1/c$ ,  $a = 8.295$  (2),  $b = 12.766$  (3),  $c = 11.831$  (3) Å,  $\beta = 123.35$  (2)°,  $V = 1046.5$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.517$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 1.328$  mm<sup>-1</sup>,  $F(000) = 486$ ,  $T = 295$  K and  $R = 0.029$  for 2509 observed reflections. The Tc atom is located on an inversion centre. The Tc—P distance is 2.541 (1) Å while the Tc—Cl bonds are 2.334 (1) and 2.331 (1) Å. Triethylphosphonium pentachloro(triethylphosphine)technetate, (III),  $M_r = 513.50$ , orthorhombic,  $Pca2_1$ ,  $a = 19.456$  (20),  $b = 10.223$  (6),  $c = 22.833$  (12) Å,  $V = 4541$  (6) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.502$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 1.33$  mm<sup>-1</sup>,  $F(000) = 2088$ ,  $T = 295$  K and  $R = 0.086$  for 2000 observed reflections. There are two independent Tc atoms in the unit cell. The Tc—Cl bonds located in *trans* positions to the phosphine ligand are 2.414 (9) and 2.365 (8) Å while the *cis* bonds vary from 2.319 (9) to 2.360 (8) Å. The Tc—P bond distances are 2.493 (8) and 2.499 (8) Å.

**Introduction.** The chemistry of technetium has recently become very important, especially in relation to the use of the isotope <sup>99m</sup>Tc in nuclear medicine as organ-imaging agents. The quantity of <sup>99m</sup>Tc needed in radiopharmacy is a few nanograms and for this reason its toxicity is negligible. It is therefore an ideal nucleus for diagnostic studies in nuclear medicine. It has been used for several years for bone scanning and recently it has been used to study the heart, the brain, the kidneys, the liver and other organs and also tumour tissue. A good review on medical diagnostic imaging with complexes of <sup>99m</sup>Tc has been published by Clarke & Podbielski (1987).

We have recently started a project on the synthesis of new technetium compounds, especially mixed-ligand complexes. We have prepared several phosphine compounds as starting material for these syntheses. Since small quantities of reactants are used in the reactions, X-ray diffraction is an excellent method of characterizing the Tc compounds when adequate crystals can be prepared. We have recently reported a study of the reactions of NH<sub>4</sub>TcO<sub>4</sub> with triphenylphosphine in different conditions (Rochon, Melanson & Kong, 1991). We have now prepared some complexes with less bulky phosphines. The crystal structures of three of these compounds are reported below. These Tc<sup>IV</sup> compounds are *trans*-Tc[P(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]Cl<sub>4</sub> (I), *trans*-Tc[P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub>Cl<sub>4</sub> (II) and [P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>H][Tc{P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>}Cl<sub>3</sub>] (III).

**Experimental.** Ammonium pertechnetate (NH<sub>4</sub>-<sup>99</sup>TcO<sub>4</sub>) was obtained from Oak Ridge National

Laboratory. It was recrystallized in nitric acid (caution: ammonium pertechnetate in acid medium will produce a radioactive volatile compound) and dissolved in water. A 0.286 M solution was prepared. All manipulations were made in a laboratory approved for low-level radioactive material (<sup>99</sup>Tc is a  $\beta$ -emitter with a particle energy of 0.292 MeV and a half-life of  $2.13 \times 10^5$  y). Triethylphosphine and methyldiphenylphosphine were bought from Aldrich.

The magnetic susceptibility measurements of the Tc compounds were performed by the Faraday method on a Cahn instrument equipped with a millibalance. Corrections were made for diamagnetism. The infrared spectra were measured in the solid state as Nujol mull on a FT-50 Digilab instrument equipped with a CsI beamsplitter.

(I). This compound was prepared by a method similar to the one described earlier by Mazzi, de Paoli, di Bernardo & Magon (1976). 1 ml of ammonium pertechnetate (0.286 M) was added to a solution containing 1 ml of conc. HCl and 15 ml of ethanol. The solution became yellow immediately. Methyldiphenylphosphine (0.5 ml) was added and the mixture was stirred overnight at room temperature. The next day, the solution was refluxed for 15 min and cooled to room temperature. The green precipitate was collected by filtration and the compound was washed twice with ethanol and dried in air. The compound was recrystallized in chloroform and green crystals suitable for diffraction methods were obtained. (I) yield  $\approx 60\%$ . IR (cm<sup>-1</sup>):  $\nu(\text{Tc—Cl})$ , 346; main other bands: 888, 740, 629, 503 and 447. Magnetic moment  $\mu = 4.1$  BM ( $3.802 \times 10^{-23}$  JT<sup>-1</sup>).

(II) and (III). 2 ml of ammonium pertechnetate (0.286 M) were added to a solution containing 4 ml of conc. HCl and 25 ml of ethanol. Triethylphosphine (3 ml) was added and the mixture was refluxed for 2 h. The mixture was left standing overnight at room temperature. The next day, there was a precipitate of yellow and green crystals. The precipitate was collected by filtration and washed several times with an ethanol-HCl solution (10 ml of ethanol and 3 ml 6M HCl). The compound was dried in air and ether added. The green compound dissolved but the yellow compound is insoluble in the ether. The green complex (II) was recrystallized in ether, while the yellow compound (III) was recrystallized in benzene. (II) yield  $\approx 20\%$ , IR (cm<sup>-1</sup>):  $\nu(\text{Tc—Cl})$  338; main other bands, 1414, 1258, 1035, 758, 725, 704 and 240; (III) yield  $\approx 50\%$ , IR (cm<sup>-1</sup>):  $\nu(\text{Tc—Cl})$  330 and 284; main other bands, 1400, 1260, 1036, 874, 760 and 723.

*Crystallographic measurements and structure resolution.* The three crystals (I), (II) and (III) were selected after examination under a polarizing microscope for homogeneity. The unit-cell parameters

Table 1. *Experimental details of the X-ray studies of (I), (II) and (III)*

	(I)	(II)	(III)
Formula	C <sub>26</sub> H <sub>26</sub> Cl <sub>4</sub> P <sub>2</sub> Tc	C <sub>12</sub> H <sub>30</sub> Cl <sub>4</sub> P <sub>2</sub> Tc	C <sub>12</sub> H <sub>31</sub> Cl <sub>3</sub> P <sub>2</sub> Tc
Crystal size (mm)	0.35 × 0.24 × 0.18	0.52 × 0.40 × 0.21	0.49 × 0.49 × 0.08
2θ max (°)	55	60	60
Quadrants	$h \pm k \pm l$	$h, k, \pm l$	$h, k, l$
$h, k, l$	0→11 $l$ , -12→12, -12→12	0→11, 0→17, -13→13	0→27, 0→14, 0→32
Scan technique	2θ/θ	2θ/θ	2θ/θ
Standard reflections, variation (%)	014, 14 $\bar{1}$ , 40 $\bar{3}$ , 2	1, 10, 0, 10 $\bar{6}$ , 402, 2	440, 128, 2
No. of independent reflections	3328	3398	6810
No. of observed reflections	2441, $I_{\text{net}} > 2.5\sigma$	2509, $I_{\text{net}} > 2.6\sigma$	2000, $I_{\text{net}} > 2.5\sigma$
Max. shift/e.s.d.	0.1	0.02	0.6
Min., max. Δρ (e Å <sup>-3</sup> )	-0.25, 0.55	-0.42, 0.56	-0.50, +0.71
Standard deviation (unit weight)	1.68	1.07	2.4

were obtained by least-squares refinement of the angles  $2\theta$ ,  $\omega$  and  $\chi$  for 15 well centred reflections on a Syntex *P1* diffractometer using graphite-monochromatized Mo *K*α radiation. Crystal data and other information are summarized in Table 1.\* Scan rates and data treatment have already been described (Melanson & Rochon, 1975). Corrections were made for Lorentz-polarization effects and the anomalous-dispersion terms of Tc, P and Cl were included in the calculations (Cromer, 1965).

The coordinates of the Tc atom in the three crystals were determined from the three-dimensional Patterson map and the positions of all the other non-H atoms were found by the usual Fourier methods. The centrosymmetric group *Pbcm* (No. 57) was first assumed for (III), but the structure could not be refined. The refinement with space group *Pca2*<sub>1</sub> (No. 29) was normal except for high thermal factors especially for the light atoms. The coordinates and isotropic thermal factors of the H atoms were refined for (I), while for (II) the coordinates of the H atoms were fixed at their calculated position with C—H = 0.96 Å and isotropic thermal factors fixed at 1.2 times the equivalent isotropic *U* of the C atom to which it is bonded. For (III), some H atoms could be located, others were calculated. They were fixed at their calculated positions with  $U_{\text{eq}} = 0.076 \text{ \AA}^2$ . For the methyl H atoms, at least one H was obtained from the difference Fourier map and the positions of the remaining atoms were calculated. Individual weights  $w = 1/\sigma^2(F)$  were applied. The refinement of the scale factor, coordinates and anisotropic temperature factors of all the non-H atoms converged to  $R = 0.039$  and  $wR = 0.036$  for (I), to  $R = 0.029$  and  $wR = 0.028$  for (II), and to  $R = 0.086$  and  $wR = 0.073$  for (III). The high residual *R* factors for (III) are caused by the high thermal motion of

the atoms. There were a few residual peaks [ $<0.55$  for (I),  $<0.56$  for (II) and  $<0.7 \text{ e \AA}^{-3}$  for (III)] in the close environment of the Tc atom.

The scattering curves of Cromer & Waber (1965) were used except for the H atoms (Stewart, Davidson & Simpson, 1965). The calculations were carried out on a Nicolet *SHELXTL* (Sheldrick, 1981) system for (I) and (II) and on a Cyber 830 computer for (III) with programs already described (Melanson & Rochon, 1975).

**Discussion.** We synthesized the two green Tc<sup>IV</sup> compounds *trans*-Tc(PR<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub> according to a method similar to the one described by Mazzi *et al.* (1976). These compounds were prepared by the reaction of NH<sub>4</sub>TcO<sub>4</sub> with PR<sub>3</sub> in ethanol in the presence of HCl. In a 1 to 5 ratio, the green disubstituted Tc<sup>IV</sup> compounds were prepared by these authors with dimethylphenylphosphine, diethylphenylphosphine and triphenylphosphine, while using a 1 to 15 ratio, the yellow-orange trisubstituted Tc<sup>III</sup> complex was synthesized with ligands less bulky than PPh<sub>3</sub>. In these reactions, PR<sub>3</sub> acts as the reducing agent. We have observed similar reactions with methyldiphenylphosphine, but using triethylphosphine, we have observed mainly two products, the green disubstituted compound and the yellow ionic complex [P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>H][Tc{P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>}<sub>2</sub>Cl<sub>4</sub>].

*trans*-Tc[P(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>Cl<sub>4</sub> (I). As expected, this green compound is the *trans* isomer. The magnetic susceptibility measurement confirmed that it was a *d*<sup>3</sup> Tc<sup>IV</sup> compound with three unpaired electrons ( $\mu = 4.1 \text{ BM}$ ;  $3.802 \times 10^{-23} \text{ JT}^{-1}$ ). The space group of (I) is *P1* with one molecule per unit cell. The refined atomic parameters of the structure are listed in Table 2. A labelled diagram of the molecule is shown in Fig. 1. The Tc atom is located on the inversion centre.

The bond distances and angles are shown in Table 3. The distances Tc—Cl are 2.324 (1) and 2.320 (1) Å, very close to the values observed in the literature for *trans* Tc—Cl bonds (Pearstein, Davis, Jones & Davison, 1989; Rochon, Melanson & Kong, 1991; Bandoli, Clemente & Mazzi, 1976). Tc—P is

\* Lists of structure factors, anisotropic thermal parameters, extra bond distances and angles in (III), bond distances and angles of H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53597 (64 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Positional parameters ( $\times 10^4$ ) with their e.s.d.'s and isotropic temperature factors ( $\times 10^4$ )

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

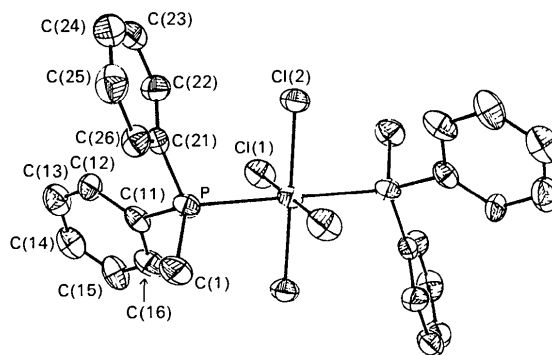
(I)	x	y	z	$U_{eq}(\text{\AA}^2)$
Tc	0	0	0	266
Cl(1)	1652 (1)	313 (1)	1534 (1)	446
Cl(2)	-2224 (1)	2754 (1)	-539 (1)	391
P	1027 (1)	1439 (1)	-2338 (1)	288
C(11)	1750 (5)	2893 (4)	-2229 (4)	311
C(12)	699 (5)	4210 (5)	-1821 (5)	439
C(22)	2554 (5)	-185 (5)	-4224 (4)	408
C(24)	5435 (6)	-2469 (6)	-3570 (5)	533
C(21)	2740 (5)	-94 (4)	-2856 (4)	324
C(23)	3910 (6)	-1389 (6)	-4564 (5)	509
C(25)	5640 (6)	-2395 (6)	-2206 (5)	494
C(16)	3298 (6)	2769 (6)	-2579 (5)	432
C(26)	4297 (5)	-1223 (5)	-1845 (5)	396
C(33)	-708 (6)	2830 (6)	-3977 (5)	431
C(13)	1208 (7)	5357 (6)	-1774 (5)	516
C(15)	3768 (7)	3940 (7)	-2516 (6)	532
C(14)	2725 (7)	5210 (6)	-2106 (5)	501
H(12)	-349 (53)	4188 (52)	-1526 (47)	578
H(13)	521 (56)	6161 (56)	-1533 (50)	476
H(22)	1596 (61)	510 (60)	-4900 (54)	604
H(1)	-1004 (63)	2021 (65)	-4041 (55)	611
H(25)	6589 (59)	-3091 (57)	-1580 (51)	478
H(26)	4468 (47)	-1222 (46)	-914 (42)	390
H(24)	6456 (52)	-3313 (51)	-3684 (46)	514
H(2)	-438 (59)	3444 (60)	-4736 (55)	444
H(14)	3059 (54)	5838 (55)	-2054 (48)	368
H(15)	4669 (62)	3885 (61)	-2763 (55)	583
H(23)	3728 (56)	-1337 (55)	-5524 (52)	538
H(3)	-1683 (68)	3549 (66)	-3707 (59)	783
H(16)	4031 (57)	1936 (57)	-2759 (50)	395

(II)	x	y	z	$U_{eq}(\text{\AA}^2)$
Tc	0	0	0	295
Cl(1)	2391 (1)	-1163 (1)	1517 (1)	453
Cl(2)	-2226 (1)	-879 (1)	275 (1)	455
P	816 (1)	1155 (1)	1997 (1)	325
C(1)	1034 (4)	411 (2)	3390 (2)	461
C(2)	1527 (5)	1052 (3)	4632 (3)	644
C(3)	3062 (3)	1890 (2)	2714 (3)	450
C(4)	4892 (4)	1224 (3)	3415 (3)	587
C(5)	-959 (3)	2177 (2)	1598 (3)	441
C(6)	-2934 (4)	1789 (3)	1215 (3)	589

(III)	x	y	z	$U_{eq}(\text{\AA}^2)$
Tc(1)	2266 (1)	-277 (2)	2000	455
Tc(2)	4743 (1)	4785 (2)	4526 (1)	465
Cl(1)	2210 (5)	-418 (10)	3054 (4)	963
Cl(2)	3353 (4)	-1302 (8)	1985 (4)	729
Cl(3)	2799 (5)	1774 (7)	2044 (5)	848
Cl(4)	1724 (4)	-2307 (8)	1895 (4)	739
Cl(5)	1215 (4)	786 (8)	1946 (4)	726
Cl(6)	3676 (4)	5852 (8)	4623 (4)	731
Cl(7)	4160 (5)	2772 (7)	4593 (4)	727
Cl(8)	5790 (4)	3686 (8)	4498 (4)	625
Cl(9)	5331 (5)	6769 (8)	4594 (4)	828
Cl(10)	4665 (5)	4874 (11)	3493 (3)	867
P(1)	2357 (5)	-238 (8)	911 (4)	536
P(2)	4845 (4)	4639 (7)	5616 (3)	433
P(3)	2317 (6)	4996 (10)	3483 (5)	874
P(4)	4903 (4)	72 (8)	3100 (3)	451
C(1)	1646 (16)	178 (28)	527 (12)	535
C(2)	968 (17)	-828 (33)	562 (17)	858
C(3)	2611 (13)	-1877 (25)	600 (14)	517
C(4)	2742 (21)	-1954 (37)	-40 (15)	1037
C(5)	2959 (15)	987 (30)	654 (13)	622
C(6)	3692 (17)	638 (27)	776 (16)	712
C(7)	3978 (16)	5100 (26)	6000 (11)	577
C(8)	3395 (14)	4250 (27)	5949 (13)	489
C(9)	5080 (15)	2958 (27)	5866 (14)	615
C(10)	5166 (15)	2974 (31)	6548 (14)	670

Table 2 (cont.)

	x	y	z	$U_{eq}(\text{\AA}^2)$
C(11)	5573 (21)	5669 (29)	5943 (15)	990
C(12)	6358 (14)	5396 (31)	5766 (16)	730
C(13)	2671 (19)	3610 (46)	3571 (18)	1322
C(14)	2325 (20)	2896 (39)	4168 (16)	1045
C(15)	2893 (17)	5750 (31)	3032 (15)	819
C(16)	3097 (17)	5130 (26)	2382 (12)	513
C(17)	1505 (17)	5042 (28)	3118 (12)	605
C(18)	1340 (18)	4194 (40)	2729 (19)	1046
C(19)	5556 (22)	-635 (42)	3569 (16)	1183
C(20)	5738 (21)	182 (37)	4027 (16)	1060
C(21)	4136 (30)	225 (43)	3318 (20)	1654
C(22)	3871 (22)	-1165 (42)	3702 (19)	1368
C(23)	5199 (19)	1697 (31)	2790 (17)	868
C(24)	4772 (22)	2234 (39)	2323 (17)	1173


 Fig. 1. Labelled diagram of *trans*-Tc(P(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>)<sub>2</sub>Cl<sub>4</sub> (I).

2.556 (1) Å. This value is close to the one [2.525 (2) Å] observed in TcCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>(CO), but longer than the ones observed for the Tc—P bonds *trans* to each other in *mer*-Tc(Me<sub>2</sub>Ph)<sub>3</sub>Cl<sub>3</sub> [2.46 (1)–2.48 (1) Å; Bandoli *et al.*, 1976] and in *mer*-Tc(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub>(DMF) [2.496 (5), 2.499 (5) Å; Rochon *et al.*, 1991]. The angles around Tc are close to the expected octahedral values. The P—C distances are normal and vary from 1.809 (4) to 1.826 (5) Å while the angles around the P atoms are close to the tetrahedral value. The Tc—P—C angles are slightly larger [110.1 (2)–116.1 (1)°] than the C—P—C values [103.5 (2)–106.7 (2)°] as observed in Tc[P(CH<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>5</sub>]<sub>3</sub>Cl<sub>3</sub> (Bandoli *et al.*, 1976) and in [Tc{P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>}Cl<sub>5</sub>]<sup>-</sup> (Bandoli, Clemente, Mazzi & Roncari, 1982; Rochon *et al.*, 1991). The average C—C distance in the phenyl rings is 1.380 (7) Å. The H atoms were refined isotropically. The average C—H distance for the aromatic rings is 0.88 (5) Å and for the methyl groups 0.92 (6) Å. The average P—C(1)—H and H—C(1)—H angles in the methyl group are 107 (3) and 111 (5)° respectively.

The packing of the molecules in the crystal is shown in Fig. 2. No hydrogen bonding is expected in this crystal. The different layers are held together only by van der Waals forces.

*trans*-Tc[P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]Cl<sub>4</sub> (II). The structure of this compound is very similar to the one described above.

Table 3. Bond distances (Å) and angles (°)

(I)			
Tc—Cl(1)	2.324 (1)	C(14)—C(15)	1.362 (8)
P—C(1)	1.815 (4)	C(21)—C(26)	1.392 (5)
C(11)—C(12)	1.392 (5)	C(24)—C(25)	1.381 (9)
C(13)—C(14)	1.349 (9)	Tc—P	2.556 (1)
C(21)—C(22)	1.390 (7)	P—C(21)	1.809 (4)
C(23)—C(24)	1.364 (6)	C(12)—C(13)	1.390 (10)
Tc—Cl(2)	2.320 (1)	C(15)—C(16)	1.392 (10)
P—C(11)	1.826 (5)	C(22)—C(23)	1.389 (7)
C(11)—C(16)	1.387 (7)	C(25)—C(26)	1.378 (6)
Cl(1)—Tc—Cl(2)	90.2 (1)	C(11)—P—C(21)	105.9 (2)
Cl(2)—Tc—P	92.7 (1)	C(13)—C(14)—C(15)	120.1 (7)
Tc—P—C(21)	113.6 (1)	C(16)—C(11)—C(12)	118.3 (5)
P—C(21)—C(22)	122.3 (3)	C(23)—C(24)—C(25)	120.4 (5)
C(1)—P—C(21)	106.7 (2)	C(26)—C(21)—C(22)	119.0 (4)
C(12)—C(13)—C(14)	121.0 (5)	Cl(2)—Tc—P	87.3 (1)
C(15)—C(16)—C(11)	120.1 (5)	Tc—P—C(11)	116.1 (1)
C(22)—C(23)—C(24)	120.3 (5)	P—C(11)—C(16)	122.4 (4)
C(25)—C(26)—C(21)	120.5 (5)	C(1)—P—C(11)	103.5 (2)
Cl(1)—Tc—P	90.5 (1)	C(11)—C(12)—C(13)	120.0 (5)
Tc—P—C(1)	110.1 (1)	C(14)—C(15)—C(16)	120.6 (6)
P—C(11)—C(12)	119.3 (4)	C(21)—C(22)—C(23)	120.0 (4)
P—C(21)—C(26)	118.7 (4)	C(24)—C(25)—C(26)	119.9 (4)
(II)			
Tc—Cl(1)	2.334 (1)	C(3)—C(4)	1.526 (4)
P—C(1)	1.822 (3)	Tc—P	2.541 (1)
Cl(1)—C(2)	1.529 (4)	P—C(5)	1.825 (3)
Tc—Cl(2)	2.331 (1)	C(5)—C(6)	1.523 (4)
P—C(3)	1.826 (3)		
Cl(1)—Tc—Cl(2)	89.4 (1)	C(3)—P—C(5)	103.0 (1)
Cl(2)—Tc—P	91.4 (1)	Cl(2)—Tc—P	88.6 (1)
Tc—P—C(5)	114.2 (1)	Tc—P—C(3)	114.3 (1)
P—C(5)—C(6)	115.3 (1)	P—C(3)—C(4)	115.0 (2)
Cl(1)—Tc—P	88.5 (1)	C(1)—P—C(5)	105.8 (2)
Tc—P—C(1)	112.4 (1)	C(1)—P—C(3)	106.1 (1)
P—C(1)—C(2)	115.5 (2)		
(III)			
Tc(1)—Cl(1)	2.414 (9)	P(1)—C(3)	1.88 (3)
Tc(1)—Cl(4)	2.340 (9)	P(2)—C(9)	1.87 (3)
Tc(2)—Cl(6)	2.354 (9)	P(3)—C(15)	1.71 (4)
Tc(2)—Cl(9)	2.334 (9)	P(4)—C(21)	1.58 (6)
P(1)—C(1)	1.69 (3)	Tc(1)—Cl(3)	2.341 (8)
P(2)—C(7)	1.95 (3)	Tc(1)—P(1)	2.493 (8)
P(3)—C(13)	1.59 (5)	Tc(2)—Cl(8)	2.327 (8)
P(4)—C(19)	1.81 (4)	Tc(2)—P(2)	2.499 (8)
Tc(1)—Cl(2)	2.360 (8)	P(1)—C(5)	1.81 (3)
Tc(1)—Cl(5)	2.319 (9)	P(2)—C(11)	1.92 (4)
Tc(2)—Cl(7)	2.354 (8)	P(3)—C(17)	1.79 (3)
Tc(2)—Cl(10)	2.365 (8)	P(4)—C(23)	1.75 (6)
Cl(1)—Tc(1)—Cl(2)	91.6 (3)	Cl(6)—Tc(2)—P(2)	90.3 (3)
Cl(1)—Tc(1)—Cl(5)	92.4 (3)	Cl(7)—Tc(2)—Cl(10)	93.9 (3)
Cl(2)—Tc(1)—Cl(4)	90.5 (3)	Cl(8)—Tc(2)—Cl(10)	92.7 (3)
Cl(3)—Tc(1)—Cl(4)	176.6 (3)	Cl(9)—Tc(2)—P(2)	87.0 (3)
Cl(4)—Tc(1)—Cl(5)	90.8 (3)	Tc(1)—P(1)—C(3)	112 (1)
Cl(6)—Tc(2)—Cl(7)	88.6 (3)	Tc(2)—P(2)—C(9)	112 (1)
Cl(6)—Tc(2)—Cl(10)	91.1 (3)	Cl(1)—Tc(1)—Cl(4)	91.6 (3)
Cl(7)—Tc(2)—Cl(9)	172.5 (3)	Cl(2)—Tc(1)—Cl(3)	90.1 (3)
Cl(8)—Tc(2)—Cl(9)	89.5 (3)	Cl(2)—Tc(1)—P(1)	86.0 (3)
Cl(9)—Tc(2)—Cl(10)	93.6 (3)	Cl(3)—Tc(1)—P(1)	89.9 (3)
Tc(1)—P(1)—C(1)	118 (1)	Cl(5)—Tc(1)—P(1)	90.1 (3)
Tc(2)—P(2)—C(7)	111 (1)	Cl(6)—Tc(2)—Cl(9)	91.3 (3)
Cl(1)—Tc(1)—Cl(3)	91.8 (3)	Cl(7)—Tc(2)—Cl(8)	90.1 (3)
Cl(1)—Tc(1)—P(1)	177.1 (3)	Cl(7)—Tc(2)—P(2)	85.5 (3)
Cl(2)—Tc(1)—Cl(5)	175.8 (3)	Cl(8)—Tc(2)—P(2)	86.0 (3)
Cl(3)—Tc(1)—Cl(5)	88.5 (3)	Cl(10)—Tc(2)—P(2)	178.5 (3)
Cl(4)—Tc(1)—P(1)	86.8 (3)	Tc(1)—P(1)—C(5)	112 (1)
Cl(6)—Tc(2)—Cl(8)	176.1 (3)	Tc(2)—P(2)—C(11)	114 (1)

The green crystals are monoclinic with space group  $P2_1/c$ . The Tc atom is located on an inversion centre resulting in a *trans* configuration of the complex. A labelled diagram of the compound is shown in Fig. 3.

The Tc—Cl bond distances are 2.334 (1) and 2.331 (1) Å while the Tc—P bonds are 2.541 (1) Å. These values are very similar to those observed in (I). The angles around the Tc atom are close to the expected octahedral values (Table 3). The Tc—P—C angles [112.4 (1)–114.3 (1)°] are slightly larger than the tetrahedral value while the C—P—C angles are slightly smaller [103.0 (1)–106.1 (1)°] as observed in the above crystal structure. The P—C bond distances [1.822 (3)–1.826 (3) Å] and the C—C bonds [1.523 (4)–1.529 (4) Å] are normal. The terminal ethyl groups are slightly flattened as shown by the high P—C—C angles which vary from 115.0 (2) to 115.5 (2)°.

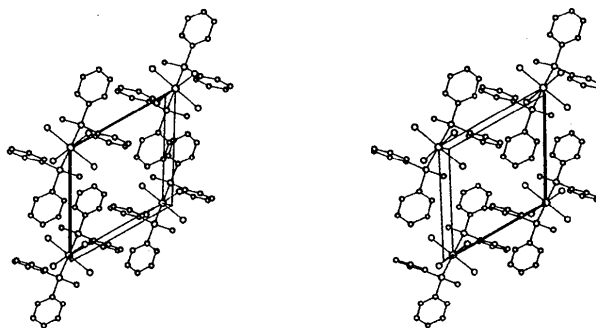


Fig. 2. Stereoscopic view of the unit cell in (I) (*b* axis vertical, down *c*\* axis).

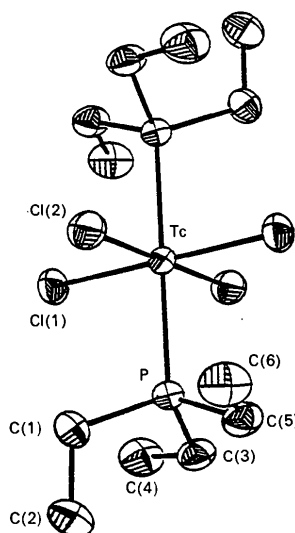


Fig. 3. Labelled diagram of (II).

The packing of the molecules in the crystal is shown in Fig. 4. No hydrogen bond is expected in this type of compound. Therefore, the molecules are held together only by van der Waals forces.

$[\text{P}(\text{C}_2\text{H}_5)_3\text{H}][\text{Tc}\{\text{P}(\text{C}_2\text{H}_5)_3\}\text{Cl}_5]$  (III). There are two independent Tc atoms in the unit cell. The bond distances and angles are listed in Table 3 (the data on the ethyl groups is part of the supplementary material). The two independent molecules are very similar. The Tc—Cl bonds located in *cis* positions to the phosphine ligand vary from 2.319 (9) to 2.360 (8) Å. The *trans* bond in one molecule seems significantly longer [Tc(1)—Cl(1) = 2.414 (9) Å], but is almost normal in the second molecule [Tc(2)—Cl(10) = 2.365 (8) Å]. These values are very similar to those observed in  $[\text{PPh}_3\text{C}(\text{CH}_3)_2\text{—CH}_2\text{—CO—CH}_3]^+[\text{Tc}(\text{PPh}_3)\text{Cl}_5]^-$  described by Bandoli *et al.* (1982). The angles around the Tc atoms are close to the octahedral values. The average *cis* Cl—Tc—Cl angle is  $91.1(3)^\circ$  while the average *cis* Cl—Tc—P angle is  $87.7(3)^\circ$ . The Tc—P bond distances are 2.493 (8) and 2.499 (8) Å, which are significantly shorter than the values observed in the two *trans*-Tc(PR<sub>3</sub>)<sub>2</sub>Cl<sub>4</sub> compounds [av. 2.549 (1) Å] described above. It seems that the *trans* influence of phosphine ligands is larger than that of chloride. The observed

Tc—P distances agree well with the values observed in *mer*-Tc[P(C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)<sub>2</sub>]<sub>3</sub>Cl<sub>3</sub> (Bandoli *et al.*, 1976).

The P—C distances in the bonded ligands are 1.85 (3) Å and the angles around the P atom are close to the tetrahedral value. The angles Tc—P—C are slightly larger [av.  $113(1)^\circ$ ] than the C—P—C angles [av.  $105(1)^\circ$ ]. The average C—C distance is 1.54 (4) Å. The ethyl groups are slightly flattened as observed by the high P—C—C angles [av.  $115(2)^\circ$ ].

The thermal factors of the atoms in the cation are very large resulting in high standard deviations on the bond distances and angles. The average bond distances and angles are: P—C = 1.71 (5), C—C = 1.54 (5) Å, P—C—C =  $115(3)^\circ$  and C—P—C =  $111(2)^\circ$ .

The presence of hydrogen bonding between the cations and the chloride ligands was investigated. The shortest P...Cl distances are 3.81 (1) and 3.77 (1) Å, but the angles C—P...Cl are not very favourable ( $75$  and  $158^\circ$ ). Therefore, hydrogen bonding is not an important stabilizing factor in this structure. The packing inside the unit cell is shown in Fig. 5. It consists of layers of cations and anions parallel to the *ab* plane.

The IR spectrum of these yellow crystals showed two  $\nu(\text{Tc—Cl})$  bands at 330 and 284  $\text{cm}^{-1}$ . For  $[\text{PPh}_3\text{C}(\text{CH}_3)_2\text{—CH}_2\text{—CO—CH}_3]^+[\text{Tc}(\text{PPh}_3)\text{Cl}_5]^-$  and  $(\text{PPh}_3\text{H})[\text{Tc}(\text{PPh}_3)\text{Cl}_5]$  (Bandoli *et al.*, 1982) two  $\nu(\text{Tc—Cl})$  bands were reported respectively at 332 and 293  $\text{cm}^{-1}$  and at 330 and 287  $\text{cm}^{-1}$ . A weak band at 2420  $\text{cm}^{-1}$  was assigned to a stretching P—H vibration as observed for the two compounds described by Bandoli *et al.* (1982).

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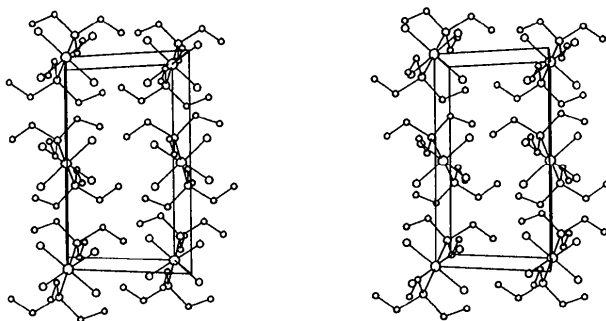


Fig. 4. Stereoscopic view of the packing in the unit cell for (II) (*b* axis vertical, down *c\** axis).

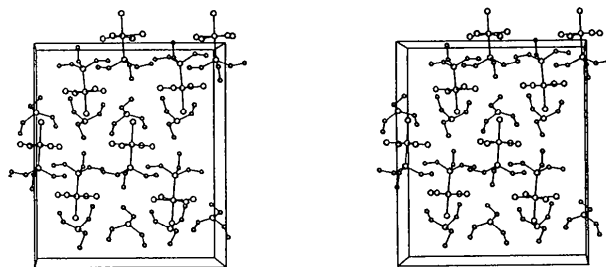


Fig. 5. Stereoscopic view of the packing in the unit cell for (III) (*c* axis vertical, *a* axis horizontal).

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