

## Technetium–Phosphine Complexes. Diethylphenylphosphonite Complexes of Technetium(III) and Mixed Ligand Complexes of Technetium(I) with Carbonyls and Diethylphenylphosphonite, and Crystal and Molecular Structure of *cis*-Dicarbonyltetrakis(diethylphenylphosphonite)technetium(I) Perchlorate

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By reaction of *trans*-[TcX<sub>2</sub>(P(OEt)<sub>2</sub>Ph)<sub>4</sub>]ClO<sub>4</sub> (X = Cl, Br, I) with carbon monoxide at room pressure, the *cis*- and *trans*-[Tc(CO)<sub>2</sub>(P(OEt)<sub>2</sub>Ph)<sub>4</sub>]ClO<sub>4</sub> isomers were obtained. To this purpose the complexes *trans*-[TcX<sub>2</sub>(P(OEt)<sub>2</sub>Ph)<sub>4</sub>]Y (X = Br, I and Y = ClO<sub>4</sub><sup>-</sup>, I<sup>-</sup>) were therefore synthesized. The formulation of all complexes is substantiated by elemental analysis, magnetic and conductivity measurements, *i.r.* and <sup>1</sup>H n.m.r. spectra and for the *cis*-isomer also by X-ray analysis. In the latter complex the technetium atom presents an octahedral coordination with some degree of distortion. The four Tc–P distances are 2.38(1), 2.41(1), 2.44(1), 2.44(1) Å, and the two Tc–CO distances are both 1.90(2) Å.

### Introduction

Mixed carbonyl phosphine complexes of technetium are not yet reported in literature. Our only reference marks are the rhenium complexes. The synthesis of rhenium complexes follows essentially two methods: the substitution of carbonyl with phosphine in the carbonyl complexes<sup>1–6</sup>, or the substitution of phosphines with carbon monoxide in the phosphine complexes<sup>7,8</sup>. In the first case the reactions are often performed under drastic conditions of temperature and pressure, only in one case<sup>6</sup> the reaction is carried out photochemically in mild conditions. In the second case the operative conditions are normal. We adopted the second method in order to study also the reactivity of the [TcX<sub>2</sub>L<sub>4</sub>]Y (X = Cl, Br, I; Y = Cl<sup>-</sup>, I<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, BPh<sub>4</sub><sup>-</sup> and L = diethylphenylphosphonite) complexes, in part already synthesized by us<sup>9</sup>, to the substitution of phosphonite with carbon monoxide. Rhenium complexes having the same formulation to those here de-

scribed are the [Re(CO)<sub>2</sub>(DFE)<sub>2</sub>]X (DFE = 1,2-bis(diphenylphosphino)ethane, and X = Cl<sup>-</sup>, I<sup>-</sup>, SnCl<sub>3</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup>) derivatives, synthesized from carbonyl complexes.

To study the change of reactivity as a function of halogen the complexes [TcX<sub>2</sub>(P(OEt)<sub>2</sub>Ph)<sub>4</sub>]Y (X = Br, I and Y = ClO<sub>4</sub><sup>-</sup>, I<sup>-</sup>) were prepared and characterized. Crystal structure of the complex *cis*-[Tc(CO)<sub>2</sub>(P(OEt)<sub>2</sub>Ph)<sub>4</sub>]ClO<sub>4</sub> was also carried out to confirm the structural data obtained from spectroscopy studies and to achieve informations about the coordination geometry of technetium atom.

### Experimental

#### Materials

Solid samples of NH<sub>4</sub>TcO<sub>4</sub> were prepared by concentration and filtration of ammonia solutions obtained from "Radiochemical Centre" Ltd., Amersham (England). The (NH<sub>4</sub>)<sub>2</sub>TcCl<sub>6</sub> was prepared by electrochemical reduction of NH<sub>4</sub>TcO<sub>4</sub> in HCl 6N on a platinum electrode<sup>10</sup>. The (NH<sub>4</sub>)<sub>2</sub>TcBr<sub>6</sub> and the (NH<sub>4</sub>)<sub>2</sub>TcI<sub>6</sub> were prepared by refluxing NH<sub>4</sub>TcO<sub>4</sub> in HBr or HI conc., respectively. The diethylphenylphosphonite was synthesized by the method of Rabinoviz and Pellon<sup>11</sup>. All the solvents used are purified and dried by standard methods.

#### Apparatus

Magnetic susceptibilities of dichloromethane solutions were measured by the Evans method<sup>12</sup> and corrected for diamagnetism of the ligands from tables given by Figgis and Lewis<sup>13</sup>. <sup>1</sup>H n.m.r. spectra were recorded on a Bruker HFX-10 instrument with TMS as internal standard. Conductivities of 10<sup>-3</sup> molar solutions in nitroethane at 25°C have been measured with a 3116B model L.K.B. conductivity bridge. Infrared spectra of nujol samples and CH<sub>2</sub>Cl<sub>2</sub> solutions with

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CsI windows were recorded on a Perkin-Elmer 621 instrument in the 4000–400  $\text{cm}^{-1}$  range, and on a Beckman I.R.11 spectrophotometer in the far infrared region (400–50  $\text{cm}^{-1}$ ).

#### Analytical Methods

The elemental analyses for the radioactive technetium was carried out by a Intertechnique Liquid Scintillation spectrometer model SL20 with Insta-gel as scintillator. The efficiency for technetium was about 97%. The halides were analyzed by potentiometrical titration with standard  $\text{AgNO}_3$  of oxidized solutions of the complexes with the Schöniger method. The perchlorate ion of carbonyl complexes was determined by conductometric titration in ethanol solutions with  $\text{AsPh}_4\text{Cl}$  as titrant.

#### Syntheses of Complexes

All the preparative work was carried out under nitrogen and with the normal health-precautions<sup>9</sup> used for radioactive technetium 99.

#### Dichlorotetrakis(diethylphenylphosphonite) technetium(III) perchlorate

The complex was synthesized following our published method<sup>9</sup>.

#### Dibromotetrakis(diethylphenylphosphonite) technetium(III) perchlorate

Diammonium hexabromotechnetate(IV) (0.5 g), diethylphenylphosphonite (6 ml) and anhydrous ethanol (40 ml) were placed in two necked roundbottomed flask equipped with condenser and inlet–outlet tube. The apparatus was flushed out with nitrogen and the reaction mixture was heated under reflux for two hours. During which time the solution became deep redviolet, but the starting solid was still present. By heating for a longer time the complex began to decompose. Then the solution was decanted and diethylphenylphosphonite (3 ml) and ethanol (20 ml) was again added to the residue. The mixture was refluxed for other two hours and the solid disappeared. A lithium perchlorate saturated solution was added to the joined together solutions to obtain a powder precipitate of  $[\text{TcBr}_2(\text{P}(\text{OEt})_2\text{Ph})_4]\text{ClO}_4$  which was recrystallized from ethanol (yield 75%).

#### Diiodotetrakis(diethylphenylphosphonite) technetium(III) iodide and perchlorate

Diammonium hexaiodotechnetate(IV) (0.5 g), diethylphenylphosphonite (4 ml) and anhydrous ethanol (30 ml) were placed in two necked roundbottomed flask equipped with inlet–outlet tube. The starting mixture was stirred at room temperature for one hour. The solution became deep green but the starting solid did not completely disappear. The residual solid was filtered away, treated with diethylphenylphosphonite

(2 ml) and ethanol (20 ml) and the mixture stirred for one hour. Addition of pentane to the joined solutions caused precipitation of a blue–green powder of  $[\text{TcI}_2(\text{P}(\text{OEt})_2\text{Ph})_4]\text{I}$ . The perchlorate salt was obtained by adding a concentrated ethanol solution of  $\text{LiClO}_4$  to a concentrated ethanol solution of the iodine salt (yield 70%).

#### Trans- and cis-dicarbonyltetrakis(diethylphenylphosphonite)technetium(I) perchlorate

These two isomers were prepared treating the halides derivatives above described in ethanol solution and in the presence of the phosphonite (0.5 M), with carbon monoxide at room pressure. We describe two cases since the complex with iodine anion requires different reaction conditions:

a)  $[\text{TcCl}_2(\text{P}(\text{OEt})_2\text{Ph})_4]\text{ClO}_4$ ,  $[\text{TcBr}_2(\text{P}(\text{OEt})_2\text{Ph})_4]\text{ClO}_4$  or  $[\text{TcI}_2(\text{P}(\text{OEt})_2\text{Ph})_4]\text{ClO}_4$  (0.5 g) reacts with CO fluxed on, if it is stirred in ethanol (20 ml) and diethylphenylphosphonite (2 ml) at 50 °C for 30 or 8 hours for the chloro- or the bromo-derivative respectively. For the iodo-derivative the reaction was carried out at room temperature for 5 hours. The reaction was stopped when the red or the red–violet color of the starting solutions disappears to give a clear solution. By cooling, white crystals of *trans*- $[\text{Tc}(\text{CO})_2(\text{P}(\text{OEt})_2\text{Ph})_4]\text{ClO}_4$  precipitated (yield 45%).

The mother liquor, treated with pentane, separated a white powder of crude *cis*- $[\text{Tc}(\text{CO})_2(\text{P}(\text{OEt})_2\text{Ph})_4]\text{ClO}_4$  impure with about the 2% of *trans*-isomer. This product was purified by dissolving it in a small amount of boiling ethanol and by adding pentane to the cooled and filtered solution. The impurities of *trans*-isomer so reduced to about 0.5%. The yield of crude product was about 36%, whilst the yield of final purified product was of 10%.

b)  $[\text{TcI}_2(\text{P}(\text{OEt})_2\text{Ph})_4]\text{I}$  (0.5 g) reacts with CO fluxed on, stirred in ethanol (20 ml) and diethylphenylphosphonite (2 ml) at room temperature for 5 hours. The final clear solution, treated with pentane gave a white powder of mixed isomers. The separation of the two isomers was not possible, and the relative yield in the two isomers was determined by  $^1\text{H}$  n.m.r. measurements (yield: *cis*-, 30%; *trans*-, 70%).

#### Crystal Data

The *cis*- $[\text{Tc}(\text{CO})_2(\text{P}(\text{OEt})_2\text{Ph})_4]\text{ClO}_4$  complex was recrystallized from ethanol.

Triclinic, space group  $\text{P}\bar{1}$ ;  $a = 17.708(15)$ ,  $b = 13.977(12)$ ,  $c = 10.185(10)$  Å;  $\alpha = 93.22(8)$ ,  $\beta = 90.48(9)$ ,  $\gamma = 96.13(11)^\circ$ ,  $U = 2502.2$  Å<sup>3</sup>; m.w. = 1047.3;  $D_m = 1.37$ ,  $D_c(Z = 2) = 1.39$  g cm<sup>-3</sup>,  $\lambda(\text{Mo-K}\alpha) = 0.7107$  Å;  $\mu(\text{Mo-K}\alpha) = 5.26$  cm<sup>-1</sup>. 3570 Independent observed reflections, four-circle diffractometer.

Accurate unit cell and orientation parameters were obtained by least-squares fit<sup>14</sup> for 27 values of  $\theta, \chi, \phi$  accurately measured.

### X-ray Intensity Measurements

Data were collected at room temperature for a crystal protected from the air (against the possible oxidation of Tc(I)) and mounted on the Siemens automatic single-crystal diffractometer, with the  $c$  axis nearly coincident with the  $\Phi$ -axis of the goniostat. Intensities were measured with a Na(Tl)I scintillation counter using Mo- $K\alpha$  radiation at a take-off angle of  $4.5^\circ$ . The  $\theta$ - $2\theta$  scan technique was employed, using a "five-value" measuring procedure<sup>15</sup>. A general reflection was remeasured every twenty reflections as a monitor of crystal stability and to normalize the intensities to a common basis. The monitor reflection was essentially constant with time. In the reciprocal space corresponding to  $2\theta_{\max}$  of  $44^\circ$  there were 3570 independent reflections with  $I > 2\sigma(I)$ . Lorentz and polarisation corrections were applied but not absorption corrections. The data were put on an approximately absolute scale with a Wilson plot.

The atomic scattering factors were taken from ref. 16 and values of  $\Delta f'$  and  $\Delta f''$  used to correct for anomalous dispersion in the scattering factor of technetium, phosphorus and chlorine were taken from Cromer's tables<sup>17</sup>.

### Solution and Refinement of the Structure

The structure was solved using conventional heavy-atom technique in space group  $P\bar{1}$ . The position of the technetium, chlorine and phosphorus atoms were determined from a three-dimensional unsharpened Patterson function and confirmed by least-squares refinement to  $R$  0.31. A difference Fourier synthesis phased on these atoms revealed the position for all 62 non-hydrogen atoms. Four cycles of block-diagonal least-squares refinement of the positional parameters and their isotropic temperature factors lowered the index to  $R = 0.12$ . From this point all atoms were allowed to vibrate anisotropically except for the perchlorate ion since might be disordered.

Two cycles of block-diagonal least-squares refinement, using unit weight for all reflections, decreased the  $R$  index to 0.092. At this point the weighting scheme was  $\omega^{-1} = \sum \rho_i |F_o|^{-1}$ . The number and value of the  $a_i$  parameters were re-evaluated several times during the refinement so as to give approximately constant averages of  $\omega(K|F_o| - |F_c|)^2$  for equally populated ranges of  $|F_o|$ . Four final cycles of block-diagonal least-squares refinement converged to a residual index  $R = 0.086$ . A difference-Fourier map computed at this stage showed some peaks up to a maximum of  $0.58 \text{ e}\text{\AA}^{-3}$  in the vicinity of the technetium atom position, while the highest peaks ( $0.84$ – $0.88 \text{ e}\text{\AA}^{-3}$ ) are in the vicinity of the perchlorate ion.

Positional and thermal parameters (only for perchlorate ion) are given in Table IV; anisotropic temperature factors for the cation are given in Table V. The atom numbering system used and the configura-

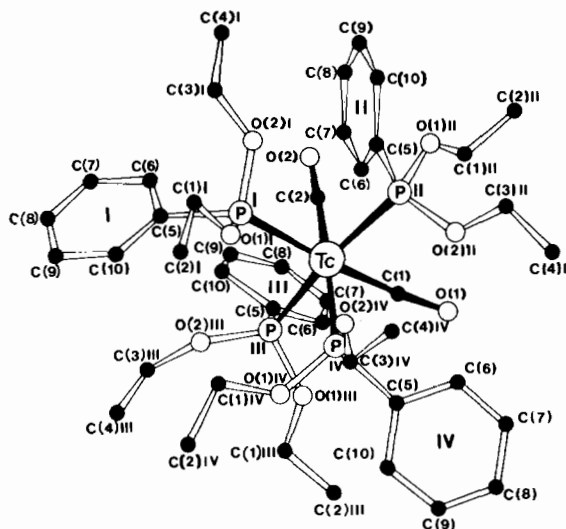


Figure 1. Three-dimensional view of the cation  $\text{cis-}[\text{Tc}(\text{CO})_2(\text{P}(\text{OEt})_2\text{Ph})_4]^+$ .

tion of the molecule are illustrated in Figure 1, while bond lengths and bond angles with their estimated standard deviations are listed in Table VI and VII respectively.

Equations of the principal planes and the deviations of atoms therefrom are given in Table VIII; Table IX shows interligand (phosphine) contacts within the same molecule; the observed and calculated structure factors are given in Table X.

The solution and refinement of the structure were carried out by use of the Crystal Structure Calculations System 'X-Ray '70<sup>18</sup>. Calculations were done on the Consorzio Interuniversitario dell'Italia Nord-Orientale, Casalecchio (Bologna), CDC 6600 computer.

## Result and Discussion

### Haloderivatives

By reaction of  $(\text{NH}_4)_2\text{TcX}_6$  ( $X = \text{Cl}, \text{Br}, \text{and I}$ ) with an excess of diethylphenylphosphonite in ethanol, the complexes of technetium(III)  $[\text{TcX}_2(\text{P}(\text{OEt})_2\text{Ph})_4]\text{Y}$  ( $X = \text{Cl}, \text{Br}, \text{I}, \text{and Y} = \text{Cl}^-, \text{I}^-, \text{BPh}_4^-, \text{ClO}_4^-$ ) were formed. The chloro complexes are reported elsewhere<sup>9</sup>; the bromo derivative was obtained as solid only with perchlorate anion. These complexes are air stable in the solid state, but in polar solvent solutions their stability might be held by means of free ligand (about  $0.5M$ ). The conductivity measurements (Table I) of  $10^{-3}M$  nitromethane solutions at  $25^\circ\text{C}$  indicate that these compounds are 1:1 electrolytes. The magnetic moment data are in good agreement with two unpaired electrons in the technetium(III) octahedral complexes. A lower value than the expected 3.2 B.M. can be explained with a deviation from the octahedral

TABLE I. General Properties of Complexes.<sup>a</sup>

Compound	Colour	X%		Tc%		$\lambda_{\text{eq}}$	$\mu_{\text{eff}}$
		Calc.	Found	Calc.	Found		
[TcCl <sub>2</sub> L <sub>4</sub> ]ClO <sub>4</sub>	red	10.02	9.82	9.32	9.35	75.9	2.6
[TcBr <sub>2</sub> L <sub>4</sub> ]ClO <sub>4</sub>	red-violet	13.89 <sup>b</sup>	13.34	8.60	8.42	70.4	2.5
[TcI <sub>2</sub> L <sub>4</sub> ]I	green	29.93	29.15	7.78	7.69	68.5	2.3
[TcI <sub>2</sub> L <sub>4</sub> ]ClO <sub>4</sub>	green	20.39 <sup>b</sup>	20.02	7.95	7.80	71.6	2.4
<i>trans</i> -[Tc(CO) <sub>2</sub> L <sub>4</sub> ]ClO <sub>4</sub>	white	9.50 <sup>c</sup>	9.42	9.46	9.41	93.8	
<i>cis</i> -[Tc(CO) <sub>2</sub> L <sub>4</sub> ]ClO <sub>4</sub>	white	9.50 <sup>c</sup>	9.48	9.46	9.39	80.2	

<sup>a</sup> L = P(OEt)<sub>2</sub>Ph. <sup>b</sup> Excluding perchlorate anion. <sup>c</sup> X = ClO<sub>4</sub><sup>-</sup> %.

geometry, especially for the iodine derivatives. Far i.r. spectra data confirm the presence of two halogens in *trans*-position (Table II).

### Carbonyl Complexes

Ethanol solutions of the dihalogenotetrakis(diethylphenylphosphonite)technetium(III) complexes [TcX<sub>2</sub>L<sub>4</sub>]ClO<sub>4</sub> (X = Cl, Br, I and L = P(OEt)<sub>2</sub>Ph) take up CO at 1 atm with the disappearance of deep colours to give clear solutions of the two isomers *cis*- and *trans*-[Tc(CO)<sub>2</sub>L<sub>4</sub>]ClO<sub>4</sub>. The starting solutions are 0.5M in the diethylphenylphosphonite because of the decomposition of halogenocomplexes. The CO substitution reactivity of the halogenoderivatives increases in the series Cl < Br < I. The relative yield in the two isomers is *ca.* 40% for *cis*- and 60% for *trans*- and seems to not drastically change with the halogeno complexes.

The reaction rate and the yield in the two isomers change with the ligand free concentration and precisely, increasing the concentration, the reaction rate and the yield in the *cis*-isomer decrease.

These qualitative informations will be substantiated by further studies and will be the subject of another communication. The two dicarbonyl complexes are air stable in the solid state and in solution of organic polar solvents such as acetone, 1,2-dichloroethane, dichloromethane, nitromethane et so on. Their are diamagnetic

and this is consistent with a *d*<sup>6</sup> spin-paired configuration in octahedral environment and 1:1 electrolytes in nitromethane solutions. The infrared and <sup>1</sup>H n.m.r. spectra are in agreement with the formulation based on elemental analysis (Table I) and indicate the presence of the phosphine ligands, ClO<sub>4</sub><sup>-</sup> anion and two terminal carbonyl groups.

### Infrared and <sup>1</sup>H n.m.r. Spectra

The structure of [TcCl<sub>2</sub>L<sub>4</sub>] complex has been shown by single crystal X-ray analysis<sup>9</sup> to be lightly distorted octahedral with the two chlorine in *trans*-position, also the far i.r. measurements are in agreement with X-ray result. By analogy one can assume that the bromo and iodo derivatives has a *trans*-configuration. The i.r. spectra in the region of stretching (Tc-X) show only a band for [TcBr<sub>2</sub>L<sub>4</sub>]ClO<sub>4</sub> and two near bands for the iodo complexes (Table II). We can assume also for the [TcI<sub>2</sub>L<sub>4</sub>]Y (Y = I<sup>-</sup> or ClO<sub>4</sub><sup>-</sup>) complexes a *trans*-configuration but in more distorted octahedron.

The structure of carbonyl complexes are substantiated by i.r., <sup>1</sup>H n.m.r. and for the *cis*-isomer by X-ray analysis. The [Tc(CO)<sub>2</sub>L<sub>4</sub>]ClO<sub>4</sub> complex, obtained by cooling the clear final solution, shows two bands in the i.r. spectra but the first one should not be fundamental and the explanation could be the same given by us<sup>19</sup> about cobalt carbonyl complexes. So, we can assume the *trans*-configuration for this isomer. Further support is given by the <sup>1</sup>H n.m.r. spectra (Table III).

TABLE II. I.r. Spectral Data of the Complexes.

Compound	$\nu(\text{Tc-X})$		$\nu(\text{C-O})$
	Solid	Solid	CH <sub>2</sub> Cl <sub>2</sub> Solution
[TcCl <sub>2</sub> L <sub>4</sub> ]ClO <sub>4</sub>	346		
[TcBr <sub>2</sub> L <sub>4</sub> ]ClO <sub>4</sub>	275		
[TcI <sub>2</sub> L <sub>4</sub> ]I	237-222		
[TcI <sub>2</sub> L <sub>4</sub> ]ClO <sub>4</sub>	239-223		
<i>trans</i> -[Tc(CO) <sub>2</sub> L <sub>4</sub> ]ClO <sub>4</sub>		2028(w)	
		1937(vs)	1946(s)
<i>cis</i> -[Tc(CO) <sub>2</sub> L <sub>4</sub> ]ClO <sub>4</sub>		1933(s)	2009(s)
		1939(s)	1954(s)

TABLE III. <sup>1</sup>H n.m.r. Spectral Data for the Two Carbonyl Isomers<sup>a</sup>.

Compound	Phenyl Protons	Methylene Protons	Methyl Protons
<i>trans</i> -[Tc(CO) <sub>2</sub> L <sub>4</sub> ]ClO <sub>4</sub>	7.4 (m)	3.6 (q)	1.22 (t)
<i>cis</i> -[Tc(CO) <sub>2</sub> L <sub>4</sub> ]ClO <sub>4</sub>	7.5 (m)	3.7 (m)	1.24 (t)
			1.26 (t)

<sup>a</sup> The spectra were measured in CDCl<sub>3</sub> unless otherwise stated. m = multiplet, q = quartet, t = triplet.

In fact this complex exhibits a 1:2:1 triplet ( $J = 7$  Hz), centered at 1.22  $\delta$ , due to the resonance of methyl protons of diethylphenylphosphonite split by methylene protons, and suggesting that the four phosphine ligands are magnetically and hence stereochemically equivalent. This indicates that the four phosphine ligands are in *trans* position, and that the "virtual" coupling between the four phosphorus nuclei is so small that it cannot be observed. The  $[\text{Tc}(\text{CO})_2\text{L}_4]\text{ClO}_4$  complex, instead, obtained by adding pentane, shows in the i.r. spectra two strong bands with the same intensity in the carbonyl region (Table II). From the Räckziegel and Bigorgne<sup>20</sup> equation:

$$I_{\text{antisym.}}/I_{\text{sym.}} = 1 - \cos\delta/(1 + \cos\delta)$$

the CO-Tc-CO bond angle ( $\delta$ ) is found to be about 90°; these results suggest a structure *cis*- for this complex.

Also the <sup>1</sup>H n.m.r. spectra of this complex support this structure. The resonance lines of phosphonite methyl protons appear as two 1:2:1 triplet ( $J = 7$  Hz) at 1.24 and 1.26  $\delta$  with the same intensity. This is in accordance with the phosphine ligands two to two equivalent.

#### X-ray Structural Analysis

The main result of the structural analysis is to have demonstrated unequivocally that the nature of the isomerism is of the type *cis-trans*, thus allowing the use of much faster methods (like i.r. and n.m.r.) for predicting and extending the geometrical structure of technetium complexes.

The structure consists of discrete monomeric octahedral cations of *cis*- $[\text{Tc}(\text{CO})_2(\text{P}(\text{OEt})_2\text{Ph})_4]^+$ , the least Tc-Tc separation being 9.90 Å, and perchlorate anions. The technetium atom presents an octahedral coordination with some degree of distortion (Figure 1, Table VII, VIII); the angles between the planes (1)-(2)-(3) are not very different from 90° as required by ideal octahedron. The PII-Tc-PIII angle is the *trans*-angle which differs more significantly from the appropriate rectilinear value; moreover, since the plane (3) is the only plane with significant deviations, practically the major part of the distortion can be ascribed

TABLE IV. Final Fractional Co-ordinates ( $\times 10^4$ ) with Standard Deviations in Parentheses and Isotropic Temperature Factor ( $\text{\AA}^2 \times 10^4$ ) for Perchlorate Ion.

Atom	x/a	y/b	z/c	U
Tc	2197(1)	2235(1)	-1271(2)	
PI*	3351(3)	3355(4)	-980(5)	
PII	1423(3)	3538(3)	-861(5)	
PIII	2781(3)	783(4)	-1551(5)	
PIV	2173(3)	2310(4)	-3657(5)	
C(1)	1282(12)	1384(14)	-1348(19)	

TABLE IV. (Cont.)

Atom	x/a	y/b	z/c	U
O(1)	712(8)	890(10)	-1381(15)	
C(2)	2276(12)	2152(12)	583(21)	
O(2)	2323(8)	2087(11)	1740(13)	
O(1)I	3540(7)	3979(9)	-2189(13)	
C(1)I	4072(13)	4861(15)	-2220(22)	
C(2)I	4283(16)	5018(18)	-3651(27)	
O(2)I	3194(7)	4036(8)	308(13)	
C(3)I	3726(12)	4831(15)	890(22)	
C(4)I	3583(17)	4874(19)	2368(24)	
C(5)I	4266(11)	2955(14)	-520(20)	
C(6)I	4351(13)	2653(15)	780(22)	
C(7)I	5043(14)	2350(17)	1148(23)	
C(8)I	5628(14)	2290(18)	254(25)	
C(9)I	5539(12)	2583(16)	-1092(25)	
C(10)I	4848(11)	2902(15)	-1462(21)	
O(1)II	995(8)	3550(9)	519(14)	
C(1)II	514(16)	2717(16)	955(27)	
C(2)II	-103(17)	3044(24)	1786(34)	
O(2)II	758(8)	3480(10)	-1965(13)	
C(3)II	171(13)	4145(16)	-1946(24)	
C(4)II	-347(19)	3886(31)	-3009(34)	
C(5)II	1787(11)	4811(14)	-785(22)	
C(6)II	2045(13)	5216(14)	-1961(25)	
C(7)II	2322(13)	6173(15)	-1918(26)	
C(8)II	2336(13)	6758(15)	-766(31)	
C(9)II	2086(15)	6320(17)	423(31)	
C(10)II	1792(12)	5351(13)	426(24)	
O(1)III	2357(8)	135(9)	-2753(13)	
C(1)III	2569(16)	-787(16)	-3236(25)	
C(2)III	1909(15)	-1325(20)	-3916(30)	
O(2)III	3676(8)	898(8)	-1897(15)	
C(3)III	4234(15)	159(18)	-1832(35)	
C(4)III	4697(16)	208(21)	-2999(35)	
C(5)III	2687(12)	35(13)	-185(19)	
C(6)III	2005(14)	-551(15)	-61(23)	
C(7)III	1869(16)	-1073(16)	1045(28)	
C(8)III	2426(16)	-1064(17)	2074(24)	
C(9)III	3108(16)	-493(17)	1899(25)	
C(10)III	3252(16)	115(15)	826(24)	
O(1)IV	2844(9)	1927(11)	-4513(15)	
C(1)IV	3623(13)	2265(19)	-4478(24)	
C(2)IV	3967(15)	1765(25)	-5598(28)	
O(2)IV	2153(8)	3391(9)	-4094(13)	
C(3)IV	2117(17)	3615(19)	-5468(22)	
C(4)IV	1751(21)	4501(28)	-5588(30)	
C(5)IV	1389(12)	1643(16)	-4605(21)	
C(6)IV	668(13)	1855(17)	-4300(24)	
C(7)IV	38(16)	1439(21)	-5085(28)	
C(8)IV	164(16)	816(22)	-6155(28)	
C(9)IV	886(16)	618(19)	-6469(24)	
C(10)IV	1515(14)	1011(17)	-5697(21)	
Cl	3709(3)	-2591(4)	4854(6)	739
O(3)	4347(10)	-3039(13)	4368(18)	1089
O(4)	3732(13)	-1679(16)	4350(22)	1400
O(5)	3064(16)	-3082(20)	4524(27)	1819
O(6)	3717(12)	-2464(15)	6214(20)	1269

\* In all the work roman numerals refer to the four phosphine ligands.

TABLE V. Anisotropic Temperature Factors ( $\text{\AA}^2 \times 10^4$ ) for the Cation *cis*-[Tc(CO)<sub>2</sub>(P(OEt)<sub>2</sub>Ph)<sub>4</sub>]<sup>+</sup>.

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Tc	420	323	375	97	12	-2
PI	477	467	454	104	39	25
PII	504	348	623	92	71	-5
PIII	571	419	570	166	-17	-40
PIV	581	518	449	170	33	-7
C(1)	890	476	569	296	151	60
O(1)	697	660	940	-164	24	66
C(2)	863	197	736	44	176	-14
O(2)	1023	905	406	104	135	140
O(1)I	606	480	635	92	95	86
C(1)I	736	573	835	11	256	170
C(2)I	1247	748	1015	83	112	338
O(2)I	621	417	749	102	32	-130
C(3)I	624	605	832	-35	-24	-302
C(4)I	1290	1039	671	9	148	-297
C(5)I	454	620	665	150	-135	-42
C(6)I	875	507	805	186	-302	-10
C(7)I	797	809	832	150	-86	155
C(8)I	846	874	889	89	-177	85
C(9)I	533	650	1169	212	-12	-51
C(10)I	513	700	673	93	27	126
O(1)II	876	473	724	191	192	-31
C(1)II	1241	542	1233	174	714	169
C(2)II	1061	1465	1712	84	873	641
O(2)II	703	773	597	342	13	-67
C(3)II	815	755	1015	532	-191	-121
C(4)II	1211	2568	1367	1216	-324	-337
C(5)II	436	514	910	186	-1	145
C(6)II	744	339	1266	220	317	143
C(7)II	815	395	1350	152	425	286

TABLE V. (Cont.)

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(8)II	660	364	1978	111	89	147
C(9)II	965	544	1658	256	70	-182
C(10)II	688	254	1148	147	-25	-117
O(1)III	809	510	680	214	-149	-164
C(1)III	1348	537	1044	455	-345	-572
C(2)III	819	1026	1370	181	-327	-569
O(2)III	726	317	1090	145	110	-31
C(3)III	796	750	2328	526	183	160
C(4)III	907	1083	1968	423	585	-222
C(5)III	841	441	552	380	97	95
C(6)III	1114	559	776	230	122	241
C(7)III	1225	457	1243	63	141	-71
C(8)III	1405	740	721	319	47	-52
C(9)III	1316	609	970	400	-142	43
C(10)III	1335	470	895	409	-273	-78
O(1)IV	865	925	677	197	119	-65
C(1)IV	621	1202	774	72	82	-130
C(2)IV	724	2003	978	299	277	-621
O(2)IV	666	682	588	79	4	24
C(3)IV	1482	1042	522	352	91	327
C(4)IV	1774	2163	937	1174	162	728
C(5)IV	606	803	653	128	-112	-199
C(6)IV	680	865	878	165	-192	-152
C(7)IV	1005	1184	1033	-26	-232	-316
C(8)IV	1018	1399	966	147	-373	-171
C(9)IV	1168	1025	699	-5	-117	-214
C(10)IV	1086	823	473	26	-13	38

Coefficients in the temperature factor expression:  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$ .

TABLE VI. Bond Lengths ( $\text{\AA}$ ) for the Cation *cis*-[Tc(CO)<sub>2</sub>(P(OEt)<sub>2</sub>Ph)<sub>4</sub>]<sup>+</sup>, with Standard Deviations in Parentheses.

(a) Distances in the inner coordination sphere of the technetium atom:

Tc-PI	2.44(1)	Tc-PIII	2.38(1)	Tc-C(1)	1.90(2)	C(1)-O(1)	1.16(2)
Tc-PII	2.41(1)	Tc-PIV	2.44(1)	Tc-C(2)	1.90(2)	C(2)-O(2)	1.19(3)

(b) Distances in the diethylphenylphosphonite ligands:

	Ligand I	Ligand II	Ligand III	Ligand IV
P-O(1)	1.57(2)	1.60(2)	1.61(1)	1.60(2)
P-O(2)	1.62(1)	1.61(2)	1.62(2)	1.60(1)
P-C(5)	1.84(2)	1.82(2)	1.79(2)	1.82(2)
O(1)-C(1)	1.47(2)	1.46(2)	1.44(3)	1.41(3)
O(2)-C(3)	1.47(2)	1.47(3)	1.51(3)	1.45(3)
C(1)-C(2)	1.53(4)	1.48(4)	1.47(4)	1.47(4)
C(3)-C(4)	1.53(3)	1.42(4)	1.45(5)	1.47(5)

(c) Phenyl rings:

	Ligand I	Ligand II	Ligand III	Ligand IV
C(5)-C(6)	1.42(3)	1.41(3)	1.40(3)	1.38(3)
C(6)-C(7)	1.39(4)	1.37(3)	1.39(4)	1.42(4)
C(7)-C(8)	1.39(4)	1.39(4)	1.43(4)	1.39(4)
C(8)-C(9)	1.46(4)	1.44(4)	1.39(4)	1.37(4)
C(9)-C(10)	1.40(3)	1.40(3)	1.43(4)	1.40(3)
C(10)-C(5)	1.42(3)	1.41(3)	1.42(3)	1.41(3)

TABLE VII. Bond Angles (deg.) for the Cation *cis*-[Tc(CO)<sub>2</sub>(P(OEt<sub>2</sub>)Ph)<sub>4</sub>]<sup>+</sup>, with Standard Deviations in Parentheses.

(a) Angles about technetium atom:					
PI–Tc–PII	90.6(2)	PII–Tc–PIII	170.4(2)	PIII–Tc–C(1)	83.5(7)
PI–Tc–PIII	98.1(2)	PII–Tc–PIV	95.1(2)	PIII–Tc–C(2)	89.0(6)
PI–Tc–PIV	93.9(2)	PII–Tc–C(1)	87.5(7)	PIV–Tc–C(1)	90.6(6)
PI–Tc–C(1)	175.3(6)	PII–Tc–C(2)	87.8(6)	PIV–Tc–C(2)	176.5(7)
PI–Tc–C(2)	84.2(6)	PIII–Tc–PIV	88.4(2)	C(1)–Tc–C(2)	91.4(8)
(b) Angles about phosphorus atoms:					
	Ligand I	Ligand II	Ligand III	Ligand IV	
Tc–P–O(1)	113.9(5)	115.7(6)	108.3(6)	120.0(6)	
Tc–P–O(2)	104.6(5)	109.8(6)	116.3(5)	111.9(5)	
Tc–P–C(5)	122.1(7)	124.2(7)	114.5(7)	119.2(7)	
O(1)–P–O(2)	110.6(7)	105.2(8)	106.3(8)	103.3(8)	
O(1)–P–C(5)	104.1(8)	97.0(9)	104.6(8)	96.8(9)	
O(2)–P–C(5)	100.7(8)	102.6(9)	106.0(9)	103.0(9)	
(c) Other angles in diethylphenylphosphonite ligands:					
	Ligand I	Ligand II	Ligand III	Ligand IV	
P–O(1)–C(1)	127.2(1.2)	122.6(1.3)	124.2(1.4)	128.6(1.4)	
P–O(2)–C(3)	125.6(1.2)	122.9(1.3)	128.4(1.3)	122.0(1.3)	
P–C(5)–C(6)	117.8(1.5)	117.9(1.5)	118.0(1.6)	117.0(1.6)	
P–C(5)–C(10)	120.4(1.5)	119.3(1.6)	120.9(1.5)	121.8(1.7)	
O(1)–C(1)–C(2)	108.4(1.7)	109.8(2.0)	108.4(2.2)	106.4(1.9)	
O(2)–C(3)–C(4)	106.5(1.7)	109.5(2.3)	108.2(2.4)	109.8(2.1)	
(d) Phenyl rings:					
	Ligand I	Ligand II	Ligand III	Ligand IV	
C(6)–C(5)–C(10)	121.8(1.9)	122.8(1.8)	120.7(1.9)	120.8(2.0)	
C(5)–C(6)–C(7)	118.5(2.0)	118.6(2.1)	120.6(2.2)	120.0(2.2)	
C(6)–C(7)–C(8)	121.3(2.2)	122.2(2.4)	121.8(2.3)	118.9(2.5)	
C(7)–C(8)–C(9)	120.3(2.2)	118.0(2.0)	116.0(2.3)	120.9(2.5)	
C(8)–C(9)–C(10)	118.6(2.1)	121.9(2.4)	124.2(2.5)	121.1(2.3)	
C(5)–C(10)–C(9)	119.4(2.0)	116.6(2.2)	116.4(2.1)	118.2(2.2)	

TABLE VIII. Least-squares Planes with the Deviations (Å) of Relevant Atoms in Square Brackets. The equation of a plane in direct space is given by  $Px + Qy + Rz = S$ , where  $x$ ,  $y$  and  $z$  are in fractional unit cell coordinates.

Plane (1):	P	Q	R	S
Tc, PI, PII, PIII, C(1)	0.414	–2.333	10.120	–1.652
[Tc –0.06, PI 0.02, PII 0.01, PIII 0.02, C(1) 0.02, O(1) 0.08]				
Plane (2):				
Tc, PI, C(1), C(2), PIV	–11.212	11.603	0.672	0.035
[Tc 0.01, PI 0.03, C(1) 0.04, C(2) –0.05, PIV –0.04, O(1) 0.11, O(2) –0.10]				
Plane (3):				
Tc, PII, C(2), PIII, PIV	14.239	7.042	–0.007	4.643
[Tc 0.06, PII –0.12, C(2) 0.11, PIII –0.13, PIV 0.08, O(2) 0.13]				
Plane (4):				
C(5)I–C(10)I	4.596	12.428	2.355	5.497
[C(5)I 0.01, C(6)I –0.02, C(7)I 0.01, C(8)I 0.0, C(9)I 0.01, C(10)I 0.0, PI –0.02]				

TABLE VIII. (Cont.)

Plane (5):	P	Q	R	S	
C(5)II–C(10)II	16.816	–4.848	2.028	0.513	
[C(5)II 0.0, C(6)II 0.0, C(7)II 0.01, C(8)II –0.02, C(9)II 0.02, C(10)II –0.01, PII –0.01]					
Plane (6):					
C(5)III–C(10)III	–8.587	10.951	4.415	–2.338	
[C(5)III –0.01, C(6)III –0.01, C(7)III 0.02, C(8)III 0.0, C(9)III –0.03, C(10)III 0.03, PIII 0.12]					
Plane (7):					
C(5)IV–C(10)IV	0.559	11.247	–6.394	4.870	
[C(5)IV 0.0, C(6)IV 0.0, C(7)IV 0.0, C(8)IV –0.01, C(9)IV 0.01, C(10)IV –0.01, PIV 0.19]					
Angles (deg.) between the mean planes:					
(1)–(2)	87.8	(2)–(4)	55.0	(3)–(7)	61.0
(1)–(3)	87.7	(2)–(5)	39.6	(4)–(5)	85.7
(1)–(4)	82.2	(2)–(6)	22.9	(4)–(6)	46.5
(1)–(5)	75.3	(2)–(7)	57.2	(4)–(7)	53.8
(1)–(6)	70.6	(3)–(4)	39.9	(5)–(6)	56.6
(1)–(7)	45.0	(3)–(5)	51.3	(5)–(7)	73.6
(2)–(3)	87.1	(3)–(6)	86.2	(6)–(7)	72.1

TABLE IX. Interligand (Phosphine) Contacts within the Same Molecule.

I–II		II–IV	
PI–PII	3.45(1)	O2II–O2IV	3.31(2)
O1I–C6II	3.32(3)	O2II–C6IV	3.19(3)
O2I–PII	3.33(1)	C6II–O2IV	3.28(3)
O2I–C5II	3.05(2)		
O2I–C10II	3.24(3)		
I–III		III–IV	
C5I–O2III	3.20(2)	PIII–PIV	3.36(1)
C10I–O2III	3.31(2)	PIII–O1IV	3.49(2)
		O1III–PIV	3.27(1)
I–IV		O1III–O1IV	3.21(2)
O1I–PIV	3.45(1)	O1III–C5IV	3.48(3)
O1I–C1IV	3.26(3)	O2III–O1IV	3.49(2)
O1I–O2IV	3.13(2)	O2III–C1IV	3.34(3)

to the displacement of PI and PIII atoms away from PI atom, but remaining still contained in plane (1). At first this distortion appears to result only from non-bonded repulsions between the bulky ligands as suggested also by the average value of the P–Tc–P angles (93.2°), while the six P–Tc–C angles have a mean value of 87.1°. Nevertheless, an examination of Table IX suggests that the larger number of contacts are between ligand III and IV and the angle PIII–Tc–PIV is the only P–Tc–P angle less than 90°. The distortion in the cation *cis*-[Tc(CO)<sub>2</sub>(P(OEt)<sub>2</sub>Ph)<sub>4</sub>]<sup>+</sup> is less pronounced than that of the *trans*-[TcCl<sub>2</sub>(P(OEt)<sub>2</sub>Ph)<sub>4</sub>] compound<sup>9</sup>, and this difference may be due to electronic effects; in fact the Tc(II) compound has a

d<sup>5</sup> configuration with one unpaired electron, while the compound of Tc(I) has a d<sup>6</sup> spin-paired configuration. Although the technetium atom is formally Tc(I), two Tc–P (Tc–PII and Tc–PIII) distances parallel those of the just mentioned compound of Tc(II), while the remaining Tc–P bonds (*trans*- to carbonyl groups) are little longer.

The difference indicates a *trans*-influence lightly greater for carbonyl group in respect to phosphine ligand, as is normal for ligands with  $\pi$ -acceptor properties (carbon monoxide) that have in *trans*-position a ligand like diethylphenylphosphonite capable of significant  $\pi$ -interaction with transition metals<sup>21</sup>. No Tc–P distances are known in literature, so it is difficult to discuss about and to have an indication of  $\pi$  back-donation and *trans*-influence. We wish to return on this subject when other technetium–phosphine structures are completed.

The average P–C (1.82 Å), P–O (1.60 Å) and C–O (1.47 Å) distances in the diethylphenylphosphonite ligands are in accordance with the same distances found for [H<sub>2</sub>Fe(P(OEt)<sub>2</sub>Ph)<sub>4</sub>]<sup>22</sup>, [TcCl<sub>2</sub>(P(OEt)<sub>2</sub>Ph)<sub>4</sub>]<sup>9</sup> and [Ni(CN)<sub>2</sub>(P(OEt)<sub>2</sub>Ph)<sub>3</sub>]<sup>23</sup>; the same is true for the angles; the M–P–C (M = Fe, Tc, Ni) angles are always larger than regular tetrahedral values while a decrease is evident in the tetrahedral C–P–O or O–P–O angles about phosphorus atoms. The C–C distances in the ethoxy groups average 1.48 Å. A similar situation is observed in the iron (1.46 Å), nickel (1.44 Å) and technetium (1.48 Å) compounds before mentioned.

We have no intention to analyse in detail this situation because it is beyond our aims, but slight disordering of the ethoxy groups was invoked by the other authors.



TABLE X. Observed and calculated structure factors. The columns are, h, 10F<sub>o</sub>, and 10F<sub>c</sub> in electrons. Reflexions marked by asterisks are unobserved and were not included in the refinement.

Table with multiple columns containing numerical data for structure factors. The columns are labeled with h, 10F<sub>o</sub>, and 10F<sub>c</sub>. The data is organized into rows corresponding to different reflections, with some rows marked with asterisks to indicate unobserved reflections. The table is very dense and contains a large amount of numerical information.

TABLE X. (Cont.)

Table with multiple columns containing numerical data and various identifiers such as H-12.2, H-13.1, H-14.1, etc. The table is organized into several distinct sections based on these identifiers.

TABLE X. (Cont.)

Table with multiple columns of numerical data and sub-headers (e.g., H-11.1, H-11.2, H-11.3, H-11.4, H-11.5, H-11.6, H-11.7, H-11.8, H-11.9, H-11.10, H-11.11, H-11.12, H-11.13, H-11.14, H-11.15, H-11.16, H-11.17, H-11.18, H-11.19, H-11.20, H-11.21, H-11.22, H-11.23, H-11.24, H-11.25, H-11.26, H-11.27, H-11.28, H-11.29, H-11.30, H-11.31, H-11.32, H-11.33, H-11.34, H-11.35, H-11.36, H-11.37, H-11.38, H-11.39, H-11.40, H-11.41, H-11.42, H-11.43, H-11.44, H-11.45, H-11.46, H-11.47, H-11.48, H-11.49, H-11.50, H-11.51, H-11.52, H-11.53, H-11.54, H-11.55, H-11.56, H-11.57, H-11.58, H-11.59, H-11.60, H-11.61, H-11.62, H-11.63, H-11.64, H-11.65, H-11.66, H-11.67, H-11.68, H-11.69, H-11.70, H-11.71, H-11.72, H-11.73, H-11.74, H-11.75, H-11.76, H-11.77, H-11.78, H-11.79, H-11.80, H-11.81, H-11.82, H-11.83, H-11.84, H-11.85, H-11.86, H-11.87, H-11.88, H-11.89, H-11.90, H-11.91, H-11.92, H-11.93, H-11.94, H-11.95, H-11.96, H-11.97, H-11.98, H-11.99, H-11.100). Each sub-header is followed by a column of numbers, and the table continues with many more columns of data.



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