# 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

M. BIAGINI CINGI<sup>a</sup>, D. A. CLEMENTE<sup>b</sup>, L. MAGON<sup>c</sup>, and U. MAZZI<sup>b\*</sup>

<sup>a</sup> Istituto Chimica Generale, The University, Parma, Italy

<sup>b</sup> Laboratorio Chimica e Tecnologia dei Radioelementi del C.N.R., Padova, Italy

<sup>c</sup> Istituto Chimico, The University, Ferrara, Italy

Received September 10, 1974

By reaction of trans- $[TcX_2(P(OEt)_2Ph)_4]ClO_4$  (X = Cl, Br, I) with carbon monoxide at room pressure, the cis- and trans- $[Tc(CO)_2(P(OEt)_2Ph)_4]ClO_4$  isomers were obtained. To this purpose the complexes trans- $[TcX_2(P(OEt)_2Ph)_4]Y$  (X = Br, I and Y =  $ClO_4^-$ ,  $\Gamma^-$ ) 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  $[TcX_2L_4]Y$  (X = Cl, Br, I; Y = Cl<sup>-</sup>, l<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>,  $BPh_4^-$  and L = diethylphenylphosphonite) complexes, in part already synthesized by us9, to the substitution of phosphonite with carbon monoxide. Rhenium complexes having the same formulation to those here described are the  $[Re(CO)_2(DFE)_2]X$  (DFE = 1,2bis(diphenylphosphino)ethane, and X = C $\Gamma$ , 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  $[TcX_2(P(OEt)_2Ph)_4]Y$  (X = Br, I and Y =  $ClO_4^-$ , I<sup>-</sup>) were prepared and characterized. Crystal structure of the complex *cis*- $[Tc(CO)_2$  (P(OEt)\_2Ph)\_4]ClO\_4 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  $NH_4TcO_4$  were prepared by concentration and filtration of ammonia solutions obtained from "Radiochemical Centre" Ltd., Amersham (England). The  $(NH_4)_2TcCl_6$  was prepared by electrochemical reduction of  $NH_4TcO_4$  in HCl 6N on a platinum electrode<sup>10</sup>. The  $(NH_4)_2TcBr_6$  and the  $(NH_4)_2TcI_6$ were prepared by refluxing  $NH_4TcO_4$  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  $10^{-3}$  molar solutions in nitroethane at 25°C have been measured with an 3116B model L.K.B. conductivity bridge. Infrared spectra of nujol samples and CH<sub>2</sub>Cl<sub>2</sub> solutions with

<sup>\*</sup> Author to whom the correspondence should be addressed.

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 efficienty for technetium was about 97%. The halides were analyzed by potentiometrical titration with standard AgNO<sub>3</sub> of oxidized solutions of the complexes with the Shöniger method. The perchlorate ion of carbonyl complexes was determined by conductometric titration in ethanol solutions with AsPh<sub>4</sub>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 fushed 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 [TcBr<sub>2</sub> (P(OEt)<sub>2</sub>Ph)<sub>4</sub>]ClO<sub>4</sub> 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 pentanc to the joined solutions caused precipitation of a blue-green powder of  $[TcI_2(P(OEt)_2Ph)_4]I$ . The perchlorate salt was obtained by adding a concentrated ethanol solution of  $LiCIO_4$  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 (0.5M), with carbon monoxide at room pressure. We describe two cases since the complex with iodine anion requires different reaction conditions:

a)  $[TcCl_2(P(OEt)_2Ph)_4]ClO_4$ ,  $[TcBr_2(P(OEt)_2Ph)_4]ClO_4$  or  $[TcI_2(P(OEt)_2Ph)_4]ClO_4$  (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*-[Tc(CO)\_2 (P(OEt)\_2Ph)\_4]ClO\_4 precipitated (yield 45%).

The mother liquor, treated with pentane, separated a white powder of crude cis-[Tc(CO)<sub>2</sub>(P(OEt)<sub>2</sub>Ph<sub>4</sub>] ClO<sub>4</sub> 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)  $[TcI_2(P(OEt)_2Ph)_4]I$  (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 <sup>1</sup>H n.m.r. measurements (yield: *cis-*, 30%; *trans-*, 70%).

## Crystal Data

The cis-[Tc(CO)<sub>2</sub>(P(OEt)<sub>2</sub>Ph)<sub>4</sub>]ClO<sub>4</sub> complex was recrystallized from ethanol.

Triclinic, space group  $P\bar{1}$ ; 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 = 2502.2Å<sup>3</sup>; m.w. = 1047.3;  $D_m = 1.37$ ,  $D_c(Z = 2) = 1.39$  g cm<sup>-3</sup>,  $\lambda$ (Mo-K $\alpha$ ) = 0.7107Å;  $\mu$ (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°. The  $\Theta$ -2 $\Theta$  scan technique was emploied, using a "fivevalue" 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° 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 heavyatom technique in space group P1. 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 nonhydrogen atoms. Four cycles of block-diagonal leastsquares 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  $\omega^{-1} = \Sigma_i a_i |F_o|^i$ . The number and value of the ai parameters were re-evaluated several time 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 blockdiagonal 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  $e^{A^{-3}}$  in the vicinity of the technetium atom position, while the highest peaks (0.84-0.88) $eA^{-3}$ ) 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 cis-[Tc(CO)<sub>2</sub>  $(P(OEt)_2Ph)_4]^+$ .

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  $(NH_4)_2TcX_6$  (X = Cl, Br, and I) with an excess of diethylphenylphosphonite in ethanol, the complexes of technetium(III) [TcX<sub>2</sub>(P(OEt)<sub>2</sub>  $Ph_4$  Y (X = Cl, Br, I, and Y = Cr, I,  $BPh_4$ ,  $ClO_4$ ) were formed. The chloro complexes are reported elsewhere9; 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 hold by means of free ligand (about 0.5M). The conductivity measurements (Table I) of  $10^{-3}M$  nitromethane solutions at  $25^{\circ}$ 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%		1	11
		Calc.	Found	Calc.	Found	eq Pren	<i>P</i> <sup>2</sup> EII
[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
trans-[Tc(CO)2L4]ClO4	white	9.50°	9.42	9.46	9.41	93.8	
cis-[Tc(CO)2L4]ClO4	white	9.50°	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 =  $ClO_4^-$ %.

geometry, expecially 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>  $L_4$ ]ClO<sub>4</sub> (X = Cl, Br, I and L = P(OEt)\_2Ph) take up CO at 1 atm with the disappearence of deep colours to give clear solutions of the two isomers *cis*- and *trans*-[Tc(CO)\_2L\_4]ClO\_4. 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 do 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 comunication. 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

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

$\nu$ (Tc–X)	ν(C–O)		
Solid	Solid	CH <sub>2</sub> Cl <sub>2</sub> Solution	
346			
275			
237-222			
239-223			
	2028(w)		
	1937(vs)	1946(s)	
	1933(s)	2009(s)	
	1939(s)	1954(s)	
	ν(Tc–X) Solid 346 275 237–222 239–223	ν(Tc-X) ν(C-O) Solid Solid 346 275 237-222 239-223 2028(w) 1937(vs) 1933(s) 1939(s)	

and this is consistent with a  $d^6$  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,  $ClO_4^-$  anion and two terminal carbonyl groups.

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

The structure of  $[TcCl_2L_4]$  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  $[TcBr_2L_4]ClO_4$  and two near bands for the iodo complexes (Table II). We can assume also for the  $[TcI_2L_4]Y$  (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  $[Tc(CO)_2L_4]CIO_4$  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 III. <sup>1</sup>H n.m.r. Spectral Data for the Two Carbonyl Isomers<sup>a</sup>.

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

<sup>a</sup> The spectra were measured in  $CDCl_3$  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 [Tc(CO)<sub>2</sub>L<sub>4</sub>]ClO<sub>4</sub> 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 Rëickziegel and Bigorgne<sup>20</sup> equation:

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

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-[Tc(CO)<sub>2</sub>(P(OEt)<sub>2</sub>Ph)<sub>4</sub>]<sup>+</sup>, the least Tc–Tc separation being 9.90Å, 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 ( $Å^2 \times 10^4$ ) for Perchlorate Ion.

Atom	x/a	y/b	z/c	U
Tc	2197(1)	2235(1)		
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  $(Å^2 \times 10^4)$  for the Cation cis-[Tc(CO)<sub>2</sub>(P(OEt)<sub>2</sub>Ph)<sub>4</sub>]<sup>+</sup>.

TABLE V. (Cont.)

	<i>U</i> <sub>11</sub>	$U_{22}$	U <sub>33</sub>	<i>U</i> <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>		<i>U</i> <sub>11</sub>	U22	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Tc	420	323	375	97	12	-2	C(8)II	660	364	1978	111	89	147
PI	477	467	454	104	39	25	C(9)II	965	544	1658	256	70	-182
PII	504	348	623	92	71	-5	C(10)II	688	254	1148	147	-25	-117
PIII	571	419	570	166	-17	-40	O(1)III	809	510	680	214	-149	-164
PIV	581	518	449	170	33	-7	C(1)III	1348	537	1044	455	-345	-572
C(1)	890	476	569	296	151	60	C(2)III	819	1026	1370	181	-327	-569
O(1)	697	660	940	-164	24	66	O(2)III	726	317	1090	145	110	-31
C(2)	863	197	736	44	176	-14	C(3)III	796	750	2328	526	183	160
O(2)	1023	905	406	104	135	140	C(4)III	907	1083	1968	423	585	-222
O(1)I	606	480	635	92	95	86	C(5)III	841	441	552	380	97	95
C(1)I	736	573	835	11	256	170	C(6)III	1114	559	776	230	122	241
C(2)I	1247	748	1015	83	112	338	C(7)III	1225	457	1243	63	141	-71
O(2)I	621	417	749	102	32	-130	C(8)III	1405	740	721	319	47	-52
C(3)I	624	605	832	-35	-24	-302	C(9)III	1316	609	970	400	-142	43
C(4)I	1290	1039	671	9	148	-297	C(10)11I	1335	470	895	409	-273	-78
C(5)I	454	620	665	150	-135	-42	O(1)IV	865	925	677	197	119	-65
C(6)I	875	507	805	186	-302	-10	C(1)IV	621	1202	774	72	82	-130
C(7)I	797	809	832	150	-86	155	C(2)IV	724	2003	978	299	277	-621
C(8)1	846	874	889	89	-177	85	O(2)1V	666	682	588	79	4	24
C(9)I	533	650	1169	212	-12	-51	C(3)IV	1482	1042	522	352	91	327
C(10)I	513	700	.673	93	27	126	C(4)IV	1774	2163	937	1174	162	728
O(1)II	876	473	724	191	192	-31	C(5)IV	606	803	653	128	-112	-199
	1241	542	1233	174	714	169	C(6)IV	680	865	878	165	-192	-152
C(2)II	1061	1465	1712	84	873	641	C(7)IV	1005	1184	1033	26	-232	-316
O(2)II	703	773	597	342	13	-67	C(8)IV	1018	1399	966	147	-373	-171
C(3)II	815	755	1015	532	-191	-121	C(9)IV	1168	1025	699	-5	-117	-214
C(4)II	1211	2568	1367	1216	-324	-337	C(10)1V	1086	823	473	26	-13	38
C(5)II	436	514	910	186	-1	145							
C(6)II	744	339	1266	220	317	143	Cœfficien	ts in th	e temper	ature fac	tor expr	ession: e	$xp[-2\pi^2$
C(7)II	815	395	1350	152	425	286	$(U_{11}h^2a^{*2})$	$+ U_{22}K$	$b^{2}b^{*2} + \cdots$	+ 20	$J_{12}h K a^*$	$b^* + \cdots$	)].

TABLE VI. Bond Lengths (Å) 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 II1	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)

# Diethylphenylphosphonite Complexes of Technetium

TABLE VII. Bond Angles (deg.) for the Cation cis	$[Tc(CO)_2(P(OEt_2)Ph)_4]^+, w$	vith Standard Deviations in Parentheses
--	---------------------------------	---

(a) Angles abo	out technetium atom:				
PI-Tc-PII	90.6(2)	PI1–Tc–PIII	170.4(2)	PIII-Tc-C(1)	83.5(7)
PI-Tc-PIII	98.1(2)	PIITcPIV	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. Learst-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): Tc, PI, PII, PIII, C(1) [Tc -0.06, PI 0.02, PII 0.01, PIII 0.02, 0	P 0.414 C(1) 0.02, O(1) 0.08]	Q -2.333	R 10.120	S -1.652
Plane (2): Tc, PI, C(1), C(2), PIV [Tc 0.01, PI 0.03, C(1) 0.04, C(2) -0.05	–11.212 , PIV –0.04, O(1) 0.11	11.603 , O(2)0.10]	0.672	0.035
Plane (3): Tc, PII, C(2), PIII, PIV [Tc 0.06, PII -0.12, C(2) 0.11, PIII -0.1	14.239 13, PIV 0.08, O(2) 0.13	7.042	-0.007	4.643
Plane (4): C(5)I-C(10)I [C(5)I 0.01, C(6)I -0.02, C(7)I 0.01, C(	4.596 (8)I 0.0, C(9)I 0.01, C(	12.428 10)I 0.0, PI –0.02]	2.355	5.497

# TABLE VIII. (Cont.)

Plane (5):		Р	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 0.0	2, C(10)II -0.01, PII -0	0.01]	
Plane (6):					
C(5)III - C(1)	0)III	-8.587	10.951	4.415	-2.338
$[\hat{C}(5)]$ III -0.0	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	3, PIII 0.12]	
• • •		, , , , , , , , , , , , , , , , , ,		. 1	
$\mathbf{D}_{1}$					
Plane (7):					
C(5)IV-C(1)	0)IV	0.559	11.247	-6.394	4.870
C(5)IV-C(1) [C(5)IV 0.0	0)IV C(6)IV 0.0, C(7)IV 0	0.559 .0, C(8)IV –0.01, C(9)IV	11.247 0.01, C(10)IV -0.01, P	6.394 IV 0.19]	4.870
C(5)IV-C(1 [C(5)IV 0.0	0)IV C(6)IV 0.0, C(7)IV 0	0.559 .0, C(8)IV –0.01, C(9)IV	11.247 0.01, C(10)IV -0.01, P	-6.394 [V 0.19]	4.870
Angles (deg	0)IV . C(6)IV 0.0, C(7)IV 0 .) between the mean pl	0.559 .0, C(8)IV -0.01, C(9)IV anes:	11.247 0.01, C(10)IV -0.01, P	-6.394 [V 0.19]	4.870
Angles (deg (1)-(2)	0)IV .C(6)IV 0.0, C(7)IV 0 ) between the mean pl 87.8	0.559 .0, C(8)IV -0.01, C(9)IV anes: (2)-(4)	11.247 0.01, C(10)IV -0.01, P 55.0	-6.394 [V 0.19] (3)-(7)	4.870 61.0
Frame (7): C(5)IV-C(1) [C(5)IV 0.0] Angles (deg (1)-(2) (1)-(3)	0)IV .C(6)IV 0.0, C(7)IV 0 .) between the mean pl 87.8 87.7	0.559 .0, C(8)IV -0.01, C(9)IV anes: (2)-(4) (2)-(5)	11.247 0.01, C(10)IV -0.01, P 55.0 39.6	-6.394 [V 0.19] (3)-(7) (4)-(5)	4.870 61.0 85.7
Plane (7): $C(5)IV-C(1 \\ [C(5)IV 0.0]$ Angles (deg (1)-(2) (1)-(3) (1)-(4)	0)IV C(6)IV 0.0, C(7)IV 0 ) between the mean pl 87.8 87.7 82.2	0.559 .0, C(8)IV -0.01, C(9)IV anes: (2)-(4) (2)-(5) (2)-(6)	11.247 0.01, C(10)IV -0.01, P 55.0 39.6 22.9	-6.394 [V 0.19] (3)-(7) (4)-(5) (4)-(6)	4.870 61.0 85.7 46.5
Plane (7): $C(5)IV-C(1 \\ [C(5)IV 0.0]$ Angles (deg (1)-(2) (1)-(3) (1)-(4) (1)-(5)	0)IV C(6)IV 0.0, C(7)IV 0 ) between the mean pl 87.8 87.7 82.2 75.3	0.559 .0, C(8)IV -0.01, C(9)IV anes: (2)-(4) (2)-(5) (2)-(6) (2)-(7)	11.247 0.01, C(10)IV -0.01, P 55.0 39.6 22.9 57.2	-6.394 [V 0.19] (3)-(7) (4)-(5) (4)-(6) (4)-(7)	4.870 61.0 85.7 46.5 53.8
Plane (7): $C(5)IV-C(1 \\ [C(5)IV 0.0.$ Angles (deg (1)-(2) (1)-(3) (1)-(4) (1)-(5) (1)-(6)	0)IV C(6)IV 0.0, C(7)IV 0 ) between the mean pl 87.8 87.7 82.2 75.3 70.6	0.559 .0, C(8)IV -0.01, C(9)IV anes: (2)-(4) (2)-(5) (2)-(6) (2)-(7) (3)-(4)	11.247 0.01, C(10)IV -0.01, P 55.0 39.6 22.9 57.2 39.9	6.394 [V 0.19] (3)(7) (4)(5) (4)(6) (4)(7) (5)(6)	4.870 61.0 85.7 46.5 53.8 56.6
Plane (7): $C(5)IV-C(1 \\ [C(5)IV 0.0.$ Angles (deg (1)-(2) (1)-(3) (1)-(4) (1)-(5) (1)-(6) (1)-(7)	0)IV C(6)IV 0.0, C(7)IV 0 ) between the mean pl 87.8 87.7 82.2 75.3 70.6 45.0	$\begin{array}{c} 0.559\\ 0.0, C(8)IV -0.01, C(9)IV\\ anes:\\ (2)-(4)\\ (2)-(5)\\ (2)-(6)\\ (2)-(7)\\ (3)-(4)\\ (3)-(5)\end{array}$	11.247 0.01, C(10)IV -0.01, P 55.0 39.6 22.9 57.2 39.9 51.3	6.394 [V 0.19] (3)(7) (4)(5) (4)(6) (4)(7) (5)(6) (5)(7)	4.870 61.0 85.7 46.5 53.8 56.6 73.6

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

I–II		II–IV	
PIPII	3.45(1)	O2II–O2IV	3.310
O1I-C611	3.32(3)	0211–C61V	3.19(
O2I–PII	3.33(1)	C6II-02IV	3.280
O2I-C5II	3.05(2)		
O2I–C10II	3.24(3)		
I–III		III–IV	
C5I-O2III	3.20(2)	PIII-PIV	3.36(
C10I–O2III	3.31(2)	PIII-O1IV	3.49(2
T TN/		O1III-PIV	3.27
<u>1–1v</u>		O1III-O1IV	3.21(2
O1I-PIV	3.45(1)	O1III-C5IV	3.48
O1I–C1IV	3.26(3)	O2III–O1IV	3.49(2
O1I-O2IV	3 13(2)	02III-C1IV	3 340

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 nonbonded 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  $d^5$  configuration with one unpaired electron, while the compound of Tc(I) has a  $d^6$  spin-paired configuration. Altough 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  $\pi$  backdonation and *trans*-influence. We wish to return on this subject when other technetium-phosphine structures are be completed.

The average P–C (1.82Å), P–O (1.60Å) and C–O (1.47Å) distances in the diethylphenylphosphonite ligands are in accordance with the same distances found for  $[H_2Fe(P(OEt)_2Ph)_4]^{22}$ ,  $[TcCl_2(P(OEt)_2Ph)_4]^9$  and  $[Ni(CN)_2(P(OEt)_2Ph)_3]^{23}$ ; 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 1.48Å. A similar situation is observed in the iron (1.46Å), nickel (1.44Å) and technetium (1.48Å) 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. Diethylphenylphosphonite Complexes of Technetium

|--|--|

	というともないないないないないないないないないないないないないないないないないないない						ığtaratıs zutesstetetetetetetetetetetetetetetetetet								2-222 1171111111111110-2016555552222 21111 1111110-2016555555552222 2222 2222 2222 2222 2222			ماريك المكانية المكانية المحالية المكانية المحالية المكانية المحالية المكانية المحالية المح	1997 - 13 - 1997		42844442548444444 488878853404444444444444444444444444444444444	11/1/1/1/1/1/1/1/1/1/1/1/1/1/1/1/1/1/1	84444444444444444444444444444444444444		tisseliseeliseeliseeliseeliseeliseelisee
12 179+ 13 226 14 183+ 15 189+ H.7.2 *16 222 *16 222 *15 305 *14 156 *13 485 *12 177+ *11 173+ *10 172+ *2	-79 5 715 6 118 7 -38 8 9 10 219 301 -123 -11 -491 -10 113 -9 74 -8 -21 -7	185+ 236 -2 1900 - 226 2 196+ 194+ - H+12+2 193+ 165 - 1855 - 179# - 187+ 165 -	-9 3 32 4 49 5 03 6 71 7 53 8 9 10 11 12 12 13 12 12 13 97 14 12 12 12 12 12 12 12 12 12 12 12 12 12	173+ 169+ 171* 312 316 489 517 239 322 188+ 284	138 - 13 - -118 - 319 - 288 - -471 - 570 - 167 - 376 - 41 - -259 -	14 169+ 13 181+ 12 161 11 173+ 10 179 -9 372- -8 163+ -7 451 -6 348 -5 492 -4 377 -3 172 -2 157+ -1 204	-148 29 212 -192 -350 -350 -430 381 -364 -369 204 -364 -364 -364 -364 -364 -364 -364 -36	-13 166 -12 169 -11 199 -11 165 -9 156 -8 157 -7 151 -6 124 -5 147 -3 146 -2 1022 -1 473 0 840	-181 206 212 -103 -16 57 175 -51 -203 -124 L1/2 -1049	-132 -112 -110 	174+ 281 1749 643 645 2163+ 2163+ 2163+ 2163+ 2163+ 2163+ 2163+ 2163+ 2163+ 2163+ 2163+ 2163+ 2163+ 2163+ 2163+ 2163+ 2163+ 2164+ 216+ 216+ 216+ 216+ 216+ 216+ 216+ 216	-)27 -299 )12 -646 -516 -99 518 -160 -814 -359 -359	 159+ 166+ 1615 4054 478 453 466 178 178+ 178+	146 - 991 - 3654 - 457 - 456 - 456 - 456 95 95	567 87654321	189 196 196 185 189 187 187 187 187 187 194 194 194 194 194	-192 -36 100 -132 127 -135 -235 -135 176 56	210123456789011	237 703 1633 322 423 423 423 423 423 423 423 1623 143 1623 1434 182- 189	-284 -689 114 -315 24207 -415 24207 -237 -201	876543210123454	518 271661206319710-	51862 -2962 18175 -2707 -2707 -2709 -2709 -429 -429 -429 -429 -429	 517 514 1562 1562 1566 1586 120 2026 1588 120 2026 1588 120 2026 1588 120 2026 1588 120 2026 1588 120 2026 120 120 120 120 120 120 120 120 120 120	+98 -525 -216 498 109 -2958 -1028 -0549 -1074 -1374 -1016 -329 -1120 -1120

TABLE X. (Cont.)

149

 $\begin{array}{c} 261 \\ -261 \\ -107 \\ -33 \\ -267 \\ -33 \\ -267 \\ -33 \\ -33 \\ -267 \\ -33 \\ -33 \\ -267 \\ -33 \\ -33 \\ -267 \\ -33$ 

-114 -110

-204 -291 313 -115 -243 -114 228 259 -292 -76 106 -32 -329 -119 -50 543218123456789812234 - /11 - /11 - 405 - 405 - 405 - 110 - 405 - 110 - 368 - 376 - 235 - 721 - 225 - 425 - 32101234567892333 12345678901234 202 95 -129 -1219 -1212 -1215 -1212 -2265 -205 -205 -2 trokiousideatizedeatizedeatie jestigestigestigestigeedie eedieedie eedieedie eedieedie of and in and in and in 11109876543210123456789011234 -74 -1) -85 185 -180 -349 225 82 -202 -200 95 142 -137 -225 -276 -118 294 219 -244 -204 \$25654512 22745455554545554574575745757575554545757554545757555454575 2775545457525454575554545755554545755555 1413210457654321012345678901123 165 64 -160 89 332 -701 -224 121109876541210125456159012214 1111098765412101255556789012214 1111098765412101255556789012214 -158 124 199 -130 -216 142 390 -156 -343 51 273 133 -269 143210987454321012345678901112 100354125711824415451018868777957503 14849542201979931800092855212179455601 4850100274855 1027-1257271125 1224456018887777957503 1484954221979931800092855212179497503 12272 127127 127127 127127 127127 232 -15 -16 226 -36 -295 1479 -1407 -449 -147 -42 277 10 -176 2833 -242 -216 54 1-19 -24910 -493067 -493067 -224428 -22448 -22448 -22448 -22448 -22448 -22448 -22448 -22448 -22448 -22448 -22448 -22448 -22448 -22448 -22448 -22448 -22448 -224888 -224888 -224888 -224888 -224888 -224888 -224888 -224888 -224888 -224888 -224888 -224888 -224888 -224888 -2248888 -2248888 -2248888 -22488888 -2248888 -224888 -2248888 -224888 -224888 -224888 -123 324 -6453 1375 -2453 1375 -2453 2000 -607 7552 2448 -2512 2488 -2512 2488 -138 -2512 2488 -138 -2512 2488 -138 -2512 2488 -138 -2512 1432 ++121 ++121 ++121 ++121 ++121 ++121 ++121 ++121 ++121 ++121 ++121 ++121 ++121 ++121 ++121 ++121 ++121 ++121 ++122 ++121 ++122 ++121 ++122 ++121 ++122 ++121 ++122 ++121 ++122 ++12 ++122 ++ 273 -133 -260 61 158 174 -293 -227 733 311 -055 121 107 -427 -197 -427 -197 -422 -293 -154 32 109 87 65 4 32 11999799999999 -----10 - 87 - 5 - 5 - 5 - 5 - 10 - 2 38 -393 -149 168 355 282 -244 -119 188 265 -14 -13 -12 -14 -19 -7 -6 -5 -13

\*\*11.\*\*

Diethylphenylphosphonite Complexes of Technetium

	60	24	2 20	44 -184	6	177.	12 :	1 15	142		8.1.8		:	316	- 355	5	236	217	: !	97 162	-2	102	7		101	-	1954	-150	,	4-5-10		•		
5 1	74	244	3 20	9. 237	ž	255 -	57 /	1 175	- 235				5	198+	145	÷.	189	123	2 2	71 -293	-1	222 245	ź	186-	- 38	6	172	1.3	-3	204-	152	-6 3	984	-79
6 1	92.	27	* 31	7 278	:	530 +	14	504 0	-494	-12	175	-229		215	171	2	147.	-146		-	i	377 -373	3	35+	- 335	1	181	215	- Z	199-	26		*1 -	-140
		.110	6 24	2 - 275	- 12	331	27	1 87	569	-14	657	100		195		;	197.	-21	н.	6.9		243 -260	- :	276	-234	•	144+	,	-1	2010 .	- 70	-	36	216
٠	4.9.7		7 19	0+ -38	- îi	190.0	69	3 149-	-162	-9	183*	- 91		396	-300	÷	190-	105 .		641 489	- 1	151 152	- 2	163	144		H.4.9		ĩ	158+	- 19		45.	60
			8 20	202				4 195-	76	-	395	- 389	10	194*	127				ŝ i	98188	5	156 111	Ť	241	-226				5	195	144	-1	99.	-169
		52L	4 14	· · ·		H4.8		2 1212			1790						н.7.8		• 2	51 +540		158 -130		505.	-154		204*	150	3	1404	- 26		924	-28
-6 î	75	188	н.	-7.8	-11	189=	24	7 215	194	-5	344	104				- 4	189	204	: ::	120		1920 -112	•	1.444			228	-209	•				95.	
-5 2	20.9	234			-10	193*	97	6 195+	-151	-4	173.	-24	-11	144+	-115	-7	194.	152	î î	91. 60		175 170		H.1.4		-5	345	- 384		4		3	95.0	-25
- 1	20.	119	- 10	-62		191.	78	9 196	-190	- ?	588	->53	-10	143+	-62	-^	194.	- 36	ο i	90* -51						-4	283	278				: :	• • • • •	-175
-2 1	87-	-66	-0 22	162	-7	171 +	162	1 155		-1	178.	200		336	311	-2	145-		1 2	4] -Z16		H,-2,9	-12	199.	150	-3	310	291		195.		2	10	304
-ī i	94.0	120	-5 18	9* -76	-6	\$15	05	\$ 199.			180*		-7	253	-236	- 2	1 ***	160	5 5	3 271	- 1	164 -157		191.	-39	-1	426	-417	-i	189.	60	-		
2 1			- 19	-217	-5	343	96			1	214	20)	-6	455		- 4	189-	-19	4 Z	73 -218	-8	192+ -161	-7	259	-217	٠	144	-153	-2	187.	-113		.1.10	
2 1		114	-2 22	217	-3	256 -	65	1		5	185	-100		343	177	-	192.	-107	5 3	69 -265	-1	179. 89		189.	1.00	1	395	377	-1	208	-213	-	94.	-145
i i	59.	116	-1 17	94 59	-2	180*	-6 -1	2 205*	142		532	358	-3	194*	-163	ĩ	200-	146	7 2	24 218	-5	1844 144		246	205	5	173	-162	ĩ	204	232	-5	19.	95
÷ 2	03-	195	0 20	8 -187	-1	162+	04 -1	1 103.	-90	5	154	-120	-2	346	-346	2	317	284	8 1	94+ 33		239 -266	- 3	218	-196		149.	-90	2	198+		-		273
· · ·	•00•	110	1 1	,		311		526 0	-325	•	-87		-1	241	-253	3	145.				-1	189146	-2	302	-286	•	179	1		1010	-165	-3	91.	-144
н	++10.7		5 30	3 357	- 2	341 -	100	264	271		247		ĩ	274	283	5	189.	-36				1924 145	-1	199-	167	-		50	ŝ	195*		-1	95.	-107
			4 19	3150	3	149	03 -	7 185-	-82	•	108.	- 28	ż	313	-300		198.	127 -		•0 Z06	â	372 -390	1	1954	112								96.	45
- 1		138	5 57	-520	- 2	243	67 -	6 190-		10	2014	-118	2	197.	-143				1 2	12 215	1	404 -354	2	194.	-152		H.5.9			43-18		1	03.	160
-4 2	. 16	244	7 31	201	6	172 -	10 -	4 1404				-1,,,	5	196.	59				\$ 5	91 * +151	5	330 323		247	219	-8	198-	116	-5	202*	140	5	10	-180
-3 1	48+	-86	8 18	o• 95	,	214 -	44 -	3 324	155		H.2.8		6	1 . 7 .	-100	-/	190.	-38 -	4 i	84   66		106* 44	5	315	201	-7	288	-215		201.	83	٠	67	123
	0.6	273	10 10	-108		243	25	2 260	-261	-12	216		2	212	-215	-0	327	- 306 -	3 1	63 208	5	192136		310	-333	-6	196*	-150	- 3	100	-131	•	82 S	273
<b>0</b> 1	94	113			12	194.	87	322	326	-11	190	236	ě	171	154		216	170	2 I	894 - 797	-	230 -143		100	- 113		215	190	-1	194.	132			
1.1	94.	67			11	333 -	139	546	568	-10	168.	-92	10	250	228	- 3	109	184	0 ž	4 -223	- í	227 202	9	1920	101	- 3	144.	85	•	339	696			
1	98-	53						2 175*	16	-9	251	-268					149.	-7	iι	87 147	9	205 -160				-2	301	-295	1	194*	-17	-•	105	139
			-8 18	. 210		4,-310		177	-199	-7	411	3/3				-;	197	189	2 2	00 209	10	504 -134		A.2.4		-1	382	416	5	194*			96.	-81
۰.	-10.8		-7 21	* 232	-11	101.	41	5 306	528	~6	229	140	~U	1-3-	-13	1	219	225	4 1	78 - 75		H1.9	-17	208	159	ĩ	1994	101	4	200*	. 75	-3	10	-215
			-6 18	-150	-10	194.	75	6 175	254	- 5	212	- 389	-10	192-	75	- ÷	192.	-76	5 i	4550			-2	198	-104	2	278	-242	2	197*	-10	-2	49	
-1 2		242	-4 18	. 70		292 -	46	251	-255	-3	442		-	220	-162		173	-141	• •	21 304	-10	199= -160	-7	200*	-174	-	196*	- G	•	144.	36	-	98.	102
ò i		37	-3 29	3 357	_7	183	31	9 144.	47	-2	350	375	-7	1474	-153				á 2	99 -233		193* 63	-6	247	235	ŝ	146	100		42.10		ĩ	98.	
12	79	274	-5 18	. 86	-6	349	36 1	255 0	512	-1	175.	-44	-6	1414	97		H.9.8				-7	219 167	-5	175	179	6	202*	-8				-	1954	
5 1	63 -	1 37	- 19			251 -	60 1	1 100	-119	ĩ	178.	-116		1414	145	- 1		- 94	M			1000 -37		1909						191	112	-		2.2
- i i	95.	-88	1 17	5 15	-3	179+				ż	161.	167	-3	403	-370	- 6	214	-230	8 1	87 159		241 -226	-2	1944	163				-4	198.	-9	5		+27
			2 23	246	-2	287	50	H.8.	•	3	183	ee1	-2	146.	- 90	-1	145.	50	7 2	59 -201	-3	198. 168	+1	185	101	-6	148+	56	-3	179	-196			
			1 11	- 102	-1	202	93 59 - I		-228	:	475	- 151	-1	346	384	°.	197.	137 .	s 2	05513	-2	217 221		1910		-2	2010	-12		263				
-5 1	9] •	27	5 18	21	í	283 -	45 -1	205	-273		185+	->3	ī	282	-274				2 1	97+ 200	-1	267 -274	ż	263	-241	- 3	201.	-86		194.	-56	-4	311	-345
-4 2	10	208	6 40	•22	2	148	69 -1	242	5252	7	365	165	5	**6	-456		H8.9	, .	a i	45· -75	i	*** ***	3	192.	127	-2	195.	-73	1	394	- 384	-3		. 95
-1			7 23	220	2	205	20 -	315	272		185*		3	1430	20	- 1		-169	5 5	22 -250	2	283 310	:	198.	-775	-1	2454	112	- 1	204	1.34		201.	'n
-1 1	90.	42	9 19	-141	ŝ	175+	57 .	7 274	-250	10	260	-219	5	192+	-120	• 6	163	-187	1	93 215		144 -212		16*	-131	ĭ	283	-313		198*	130	÷	193.	-20
0 3	06	269	10 10	• •1	6	179+		6 166	-184	- 11	500.	105		505.	-148	-1	189.	101	i ż	45 247	5	300 -307	7	195.		2	248	-261	5	198.	-+1	2	200.	-148
1,1	01 -	17	н.	5.8		280	1.	2 111.					4	149.	100	ŝ	107.	116	2 2	28 -177		246 256		215	222	2	222	226		m	-128	÷.	1 2 7 4	155
3 1		229			ş	186*	ei .	172	-53					199	144	÷	166	-212	22	26 -250		216 -217	•	184.	<i>'</i> •	•	247	213						-49
_	93.	84 -	10 19	* -56	11	311 -	16 -	2 173	-211	-12	201+	128				د	100	-77	5 1	64 161		19796		н.3.9			H.7.9	•						
• i			- 27	211	- !!	192+	28 -	1 179.	-2	- 1 1	196.			H.6.8			338	323	6 1	86. 54	10	167. 46								199*	156			
5 2	01	1 99						222	1		14.7	-98	-10	1857	82	2	146.	185	! !	930 -161				123	-158		2020	-105		236				
4 1 5 2 6 1 7 1	01 • •7•	199 -67 176	-6 16	-164				1055												70 108														
5 2 1	97.	199 -67 176	-8 16 -7 17 -6 24	-164		**-2.8		2 304	-314		269	<i>č</i> 51	-9	100-	-150		47.4						-7	338	305	-2	503°	127	-3	190.	-6			
4 5 1 1 6 7 H	97. 98	-67 176	-6 24	-164 -233 -208		**-2-8		2 JOA 2 JOA 2 ZZ7	-314	-	269	251	-8	194.	-150		*****		• •		-10	200152		189*	114	-1	161	101	-2	196*	163			
4 1 2 1 1 6 7 1 H	93	-67	-8 16 -7 17 -6 24 -5 19 -4 29	-164 -233 208 359	-12	N2.8	52	2 30A 3 227 4 109*	-314 -193 200		269 185* 260	251 160 -287 -193	-9	194 194 213	-150 -106 173	-2	1000	124	т. н	3.9	-10	200* -152		338	302 114 -372	-2	203° 161 246 218	127 101 -274	-2 -2	196*	-19			
4 5 2 1 1 5 6 7 1 H -7 2 1	97. 97. 98	-83 85	-8 16 -7 17 -6 24 -5 19 -4 29 -3 18 -2 35	-164 -233 208 359 0 -11 -387	-12 -11 -12	H2.8 195+ 198+ 192+	52 52	2 30A 3 227 4 199* 5 526 6 1A7*	-314 -193 200 509 -23		269 185* 260 416 353	251 168 -287 -393 368	-9 -8 -7 6 5	190 194 213 162 182	-150 -186 173 176 -35	2	1	124 -159 -179	н н н	-3.9 09 214	-10 -9 -8 -7	200* -152 163 160 190* 62 180 -38	74547	338 189* 248 218 244	302 114 -372 -204 240	-2 -1 0 1	2030 161 246 218	127 101 -274 -106	- 2 - 2	190* 194* 191* 262 199*	-19			
4567 H -7612	97. 97. 98	-83 85 237	-8 16 -7 17 -6 24 -5 19 -4 29 -3 18 -2 35 -1 15	-164 -233 208 359 -11 -387 -112	-12 -11 -11	H2.8 195* 198* 192* 185 -	52 52 41	2 30A 3 227 4 109* 5 526 6 1A7* 7 473	-314 -193 200 509 -23 -466	******	269 185* 260 416 353 553	251 881 785- 892- 806 916		190. 194. 213 162 182. 184.	-150 -106 173 176 -35 -105	1111	192-	124 -159 -179 -33		-3.9 214 90* -171	-10	200° -152 163 160 190° 62 180 -38 188° -74	249472	338 189* 348 218 2^4 327	302 114 -372 -204 240 311	-2 -1 1	2030 161 246 218	127 101 -274 -108		194* 194* 191* 262 199* 213	143			
4567 H 2121	97. 97. 98 18.4 87. 10 87. 10 89.	-83 85 237 -61	-8 16 -7 17 -6 24 -5 19 -4 29 -3 18 -2 35 -1 15 0 18	-164 -233 208 359 -11 -387 -112 -112	-12 -11 -17 -9 -8	H2.8 195* 198* 192* 185 - 191*	52 52 61 11 67	2 30A 3 227 4 199* 5 526 6 1A7* 7 473 8 1A8*	-314 -193 200 509 -23 -466 90		269 185* 260 416 353 553 311 243	251 160 782- 893 806 510 -280		190. 194. 213 162 182. 182. 184.	-150 -104 173 176 -35 -105 -0		108. 192. 200. 144.	124 -159 -179 -33 182	· · · · · · · · · · · · · · · · · · ·	09 214 90* -171 79 -303	-10	2000 -152 163 160 1900 62 180 -38 1886 -74 259 -224	*******	338 189* 348 218 218 214 327 192*	302 114 -372 -204 240 311 42	-2	203* 161 246 218 46.1	127 101 -274 -106		190* 194* 191* 262 199* 213 196* 201*	-61 -19 -222 -101 -222 -101 -222 -201 -201 -201			
4567 H 21211	97. 97. 97. 97. 97. 97. 97. 97. 97. 97.	-83 -67 176 -83 237 -61 141 7	-8 164 -7 17 -6 24 -5 19 -4 29 -3 18 -2 35 -1 15 0 18 1 17 2 17	137 5 -164 0 -233 0 208 3 359 0 -11 0 -387 5 -112 1 -112 1 -112 1 -112 1 -112 1 -112 1 -112 1 -164 1 -233 1 -345 1 -233 1 -233 1 -233 1 -355 1 -112 1 -112 -1	-12 -11 -11 -9 -8 -7	H2.8 195* 198* 192* 185 - 191* 349 185*	52 52 11 67 59	2 30A 2 227 4 199* 5 526 6 1A7* 7 473 8 1A8* 9 218 0 198*	-314 -193 200 -23 -23 -90 207 -3	-7454321	269 185 260 416 353 553 311 283 180	251 160 -287 -393 806 510 -280 -316 -99		190 194 213 162 182 182 184 184 184 184 184 184 184 184	-150 -106 173 176 -35 -108 -0 142 230		1.41 187- 187-	124 -159 -179 -33 142 89 -115	9 8 1 2 2 1	-3.9 90° -171 79 -303 32 209 69* 200	-10987 -543	2008 -152 163 160 1908 62 166 -30 1688 -74 259 -25 1958 167 227 228	74547474707	338 189* 348 218 2^4 327 192* 406	302 114 -372 -204 240 311 42 -390 -105	-2	203* 161 246 218 46.1 194* 197*	127 101 -274 -106 0 -20 -132		190* 194* 191* 262 199* 213 196* 201* 197	-19 -19 -222 -222 -222 -222 -222 -222 -2			

The bond distances in perchlorate anion are Cl-O(3) = 1.43 Å, Cl–O(4) = 1.40 Å, Cl–O(5) = 1.30 Å and 1.39 Å, the mean dimension of O-Cl-O angle is 109.5°. Only one distance Cl-O(5) differs significantly from the expected Cl-O value (1.40Å)<sup>24</sup>, but the O(5) atom possesses the highest thermal motion (U =0.1819Å<sup>2</sup>) in the perchlorate group and many peaks in the difference Fourier synthesis are near this atom, moreover the O(5) atom is not involved in the closest intramolecular contacts of ClO<sub>4</sub><sup>-</sup> anion: O(3)-C(9)I (1-x, -y, -z) = 3.43Å, O(3)–C(2)IV(1-x, -y, -z) =3.49 Å, O(3)–C(10)I(1–x, –y, –z) = 3.30 Å, O(3)– C(2)I(x, -1+y, 1+z) = 3.47Å, O(4)-C(1)III(x, y, 1+z)= 3.48 Å, O(4)–C(8)III(x, y, z) = 3.47 Å, O(4)–C(9) III(x, y, z) = 3.32 Å, O(6)-C(1)III(x, y, 1+z) = 3.29 Å,O(6)-C(7)I(1-x, -y, 1-z) = 3.44 Å. No cation-cation approaches exist below 3.34Å, the closest intercation separation being O(2)–C(10)IV(x, y, 1+z) = 3.34Å; moreover there exists some contacts of the order of 3.5 Å between the C(5)IV-C(10)IV benzene ring with its centrosymmetrically (0,0,-1/2) related benzene ring, moreover the benzene rings are not superimposed.

# Acknowledgements

We thank Prof. A.A. Orio and Dr. G. Bandoli for the helpfull discussion on this paper, Mr. R. Salmaso, Mr. F. Benetollo and Mrs. G. Baroni for technical assistance.

M. Biagini Cingi, D. A. Clemente, L. Magon and U. Mazzi

#### References

- 1 W.J. Kirkham, A.G. Osborne, R.S. Nyholm and M.H.B. Stiddard, J. Chem. Soc., 1965, 551.
- 2 M. Freni, V. Valenti and D. Giusto, J Inorg. Nucl. Chem., 1965, 27, 2635.
- 3 M. Freni, D. Giusto and P. Romiti, J. Inorg. Nucl. Chem., 1967, 29, 761.
- 4 E.W. Abel and S.P. Tyfield, J. Can. Chem., 1969, 47, 4628.
- 5 E. Singleton, J.I. Moelwyn-Hughes and W.B. Garner, J. Organometal. Chem., 1970, 21, 449.
- 6 J.I. Moelwyn-Hughes, A.W.B. Garner and N. Gordon, J. Organometal. Chem., 1971, 26, 373.
- 7 M. Freni and V. Valenti, J. Inorg. Nucl. Chem., 1961, 16, 240.
- 8 P.G. Douglas and B.L. Show, J. Chem Soc. (A), 1969, 1491.
- 9 U. Mazzi, D.A. Clemente, G. Bandoli, L. Magon and A.A. Orio, *Inorg. Chem.*, to be published. G. Bandoli, D.A. Clemente, U. Mazzi and E. Tondello, *Cryst. Struct. Comm.*, 1974, 3, 293.
- 10 G. A. Mazzocchin, F. Magno, U. Mazzi and R. Portanova, Inorg. Chim. Acta, 1974, 9, 263.
- 11 R. Rabinowitz and J. Pellon, J. Org. Chem., 1961, 20, 4623.
- 12 D.F. Evans, J. Chem. Soc., 1959, 2003; R.A. Bailey, J. Chem. Ed., 1972, 49, 297.

- 13 D.N. Figgis and J. Lewis, "Modern Coordination Chemistry", J. Lewis and R.G. Wilkins, Eds. Interscience, New York, N.Y., 1960, p. 403.
- 14 W. R. Busing and H. A. Levy, Acta Cryst., 1967, 22, 457.
- 15 G. Bandoli, C. Panattoni, D.A. Clemente, E. Tondello, A. Dondoni and A. Mangini, J. Chem. Soc. (C), 1970, 1407.
- 16 D.T. Cromer and J.T. Waber, Acta Cryst., 1965, 18, 104.
- 17 D.T. Cromer, Acta Cryst., 1965, 18, 17.
- 18 'X-Ray '70', System of Programs University of Maryland, Technical Report, TR 646.
- 19 E. Bordignon, U. Croatto, U. Mazzi and A. A. Orio, *Inorg. Chem.*, 1973, 12, 935.
- 20 A. Rëckziegel and M. Bigorgne, J. Organometal. Chem., 1965, 3, 341.
- 21 A.A. Orio, B.B. Chastain and H.B. Gray, *Inorg. Chim.* Acta, 1969, 3, 8.
- 22 L.J. Guggenberger, D.D. Titus, M.T. Flood, R.E. Marsh, A. A. Orio and H.B. Gray, J. Am. Chem. Soc., 1972, 94, 1135.
- 23 J.K. Stalick and J.A. Ibers, Inorg. Chem., 1969, 8, 1084.
- 24 W.S. McDonald and D.W.J. Cruickshank, Acta Cryst., 1967, 22, 37.