Preparation and Structural Characterization of Salts of Oxotetrachlorotechnetium(V)

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The reduction of pertechnitate(VII) ion, TeO_4^-, in aqueous HCl by hypophosphorous acid yields a dark green solution, as has been previously reported. From this solution olive green or gray-green crystalline solids can be isolated by addition of large cations such as $(n\text{-}C_4H_9)_4N^+$ or $(Ph_3P)_2N^+$. Analytical and infrared data indicate that the anion in these crystalline solids is $TcOCl_4^-$, the tetrachlorooxotechnetate(V) ion. For the compound $[(Ph_3P)_2N][TcOCl_4]$, **1**, a complete X-ray crystallographic structure determination has been carried out to define fully the oxotechnetate anion. Compound **1** crystallizes in space group $Pna2_1$ (No. 33) with unit cell constants of $a = 21.618$ (5) Å, $b = 16.870$ (5) Å, $c = 9.658$ (3) Å, and $Z = 4$. The formula unit is the crystallographic asymmetric unit, and no crystallographic symmetry is imposed on either cation or anion. The $TcOCl_4^-$ ion is, to a first approximation, square pyramidal, as would be expected, but is appreciably distorted, mainly in the sense of having significantly different trans Cl–Tc–Cl angles, 139.2 (1) and 153.7 (1)°. The symmetry is C_{2v} within the experimental errors, with a Tc=O distance of 1.610 (4) Å and a mean Tc–Cl distance of 2.31 ± 0.01 Å. The $Ph_3PNPPh_3^+$ ion has dimensions closely resembling those previously found for it in other compounds. Both compounds show a strong infrared absorption at ca. 1015–1020 cm^{-1} which may be assigned to stretching of the short Tc=O bond. Our conclusive identification of these green crystalline products as $TcOCl_4^-$ salts is compared with previous reports in some of which a similar formulation was proposed while in others a different anionic species, $Tc_2Cl_8^{2-}$, was postulated.

Introduction

The products obtained by reduction of the TcO_4^- ion in aqueous hydrochloric acid solution have been investigated several times in the past. The earliest such study that we are aware of was reported by Busey[2] in 1959. Busey observed that TcO_4^- is reduced by 12 M HCl or by H_3PO_2 in 8 M HCl to a Tc^V species, which he characterized by its ultraviolet absorption spectrum but did not isolate in any solid compound or otherwise further characterize. The oxidation number V was established by titration with $SnCl_2$, and the suggestion was made that the Tc^V species was likely to be a monooxo anion.

In 1965 confirmation of Busey's work was reported by Jezowska-Trzebiatowska and Baluka,[3] who also obtained a green solid which was shown to be diamagnetic and to have an elemental analysis consistent with the formula $(N\text{-}H_4)_2[TcOCl_5]$. In 1971 the isolation of several other green salts of the $TcOCl_5^{2-}$ ion, with K^+ and Cs^+ as well as NH_4^+, was described,[4] and it was reported that all these have very strong infrared absorption bands, at 956 cm^{-1} for the Cs^+ salt and at ca. 990 cm^{-1} for the others; these bands were assigned to the stretching of a Tc=O bond. The electronic structure and possible assignments of the UV–visible absorption spectrum were also discussed.

It is pertinent to note that compounds containing the $ReOBr_4^-$ and $ReOCl_4^-$ ions are well-known[5] and have ν-(Re=O) bands in their infrared spectra at frequencies from 955 to 1010 cm^{-1} depending on the associated cation.

In the meantime, the reduction of TcO_4^- in aqueous HCl by metallic zinc (in the form of a Jones reductor) was reported,[6] and the products were shown to be $TcCl_6^{2-}$ (which had also been found accompanying Tc^V in the reactions discussed above) and a new species which subsequent X-ray crystallographic[7,8] and spectroscopic[9,10] work has conclusively identified as $Tc_2Cl_8^{3-}$.

Most recently, in 1977, there appeared a report[11] that by "reduction of $^{99}TcO_4^-$ with H_3PO_2 in hydrochloric acid" a dark green solution was obtained from which, upon addition of $[(n\text{-}C_4H_9)_4N]Cl$, an olive green crystalline solid was precipitated. This solid was identified as $[(n\text{-}C_4H_9)_4N]_2[Tc_2Cl_8]$, and X-ray data were cited showing it to be isomorphous with the well-established $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$.[12]

Our intense interest in obtaining a compound containing the previously unreported $Tc_2Cl_8^{2-}$ ion (instead of the $Tc_2Cl_8^{3-}$ ion) as well as the fact that the reported method or preparation seemed at variance with previous literature and with our own earlier efforts to isolate such a substance has led us to examine once more the reduction products of TcO_4^- obtained by using H_3PO_2 in concentrated HCl, with particular attention to characterizing the green solids so obtained by X-ray crystallography. We report our results here.

Experimental Section

General Information. All operations other than the collection of X-ray data were conducted in laboratories approved for medium-level radioactivity (^{99}Tc is a weak β emitter with a half-life of 2.12×10^5 years and particle energy of 0.29 MeV). All manipulations were carried out by using standard Schlenk-line apparatus or a Vacuum Atmospheres drybox. Solvents were thoroughly purged with argon or nitrogen prior to use. Infrared spectra were obtained by using either a Perkin-Elmer Model 180 grating infrared spectrophotometer or a Pye-Unicam SP 1100 spectrophotometer. Visible spectra were measured with a Cary Model 17 spectrophotometer. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Ammonium pertechnetate in aqueous solution was obtained from New England Nuclear, Billerica, Ma.

Preparation of $(Bu_4N)[TcOCl_4]$. Method 1. To a thoroughly purged 15-mL two-neck flask equipped with a magnetic stir bar were added 4.5 mL of Ar-purged 12 M hydrochloric acid and 0.7 mL of 50% w/w hypophosphorous acid (Baker) via syringes. To the stirred solution was added 3.6 mL of a 0.33 M (1.19 mmol) aqueous ammonium pertechnetate solution via a syringe. After $1^1/_2$ h stirring, the dark green solution was treated with 3.5 mL of a 75% w/w tetrabutylammonium chloride solution, precipitating a light green, microcrystalline solid which was filtered under N_2. After being washed with 2 mL of 12 N hydrochloric acid, followed by six 5-mL portions of 2-propanol, the light gray-green solid was dried under vacuum. The yield was 0.42 g, 70%. This solid was recrystallized from CH_2Cl_2/hexane to yield large green plates. Anal. Calcd for $C_{16}H_{36}NOTcCl_4$: C, 38.49; H, 7.27; N, 2.81; Cl, 28.40. Found: C, 38.42; H, 7.22; N, 2.67; Cl, 26.34, 29.74. Attempted recrystallization from methanol or acetone yielded green plates; however, upon filtration or drying, these crystals crazed and broke apart.

Method 2. Ammonium pertechnetate (0.5 g) and tetra-*n*-butylammonium bromide (1.0 g) were dissolved in 60 mL of a 1:1 mixture of H_3PO_2 (50%) and HCl (12 M), and the solution was stirred under N_2 for 3 h. The resulting green precipitate was filtered and washed with 20 mL of absolute ethanol. The gray-green solid was dissolved in CH_2Cl_2; slow evaporation of this solution in a stream of N_2 afforded large green platelets suitable for X-ray diffraction studies. Preliminary crystallographic examination of the crystals obtained by each of the two methods showed them to be identical.

Preparation of $[(Ph_3P)_2N][TcOCl_4]$. A purged round-bottom flask was charged with 0.067 g (0.13 mmol) of tetrabutylammonium oxotetrachlorotechnetate and 1.0 g of $(Ph_3P)_2N^+Cl^-$, bis(triphenylphosphin)iminium chloride, and enough methanol to dissolve both solids was added via a cannula and the pale green solution refrigerated. Slowly, dendritic green crystals formed. This solid was recrystallized from CH_2Cl_2/hexane to yield some yellow

$[(Ph_3P)_2N]_2TcCl_6$ and well-formed dark green blocks of $(Ph_3P)_2NTcOCl_4$. The yield was 0.028 g.

Spectra. The infrared spectra were recorded by using samples pressed in KBr disks. Samples of tetra-*n*-butylammonium chloride and bromide and $[(Ph_3P)_2N]Cl$ were run for comparison. In (*n*-$Bu_4N)[TcOCl_4]$ there is a strong band at 1020 ± 5 cm^{-1} and in $[(Ph_3P)_2N][TcOCl_3]$ one at 1016 ± 5 cm^{-1} which can be assigned to ν(Tc=O). In each compound there is a medium-intensity band at 375 ± 5 cm^{-1} for ν(Tc–Cl). The visible spectrum of (*n*-Bu_4N)-$[TcOCl_4]$ dissolved in methanol had a band at 775 nm with ϵ 80.

Crystallography. Air-stable olive green single crystals of $[(C_6H_5)_3PNP(C_6H_5)_3][TcOCl_4]$ obtained as described above were suitable for X-ray diffraction studies. Weissenberg and precession photographs, used to determine the probable space group and a preliminary set of lattice constants, indicated orthorhombic, *mmm*, Laue symmetry. The systematically absent reflections were those required by the centrosymmetric space group *Pnam* (an alternate setting of *Pnma*-D_{2h}^{16}; No. 62[13a]) or the noncentrosymmetric space group *Pna2$_1$-C$_{2v}^9$* (No. 33[13b]). The choice of the noncentrosymmetric space group was fully supported by all stages of the subsequent structure determination and refinement.

Intensity measurements utilized a spherical specimen 0.61 mm in diameter which was glued to the end of a thin-glass fiber with a tip diameter of 0.15 mm. This crystal was then carefully aligned on a computer-controlled Syntex $P\bar{1}$ autodiffractometer, and a total of 15 high-angle ($2\theta_{MoK\alpha} > 25°$) reflections, chosen to give a good sampling of reciprocal space and diffractometer settings, were used to align the crystal and calculate angular settings for each reflection. A least-squares refinement of the diffraction geometry for these 15 reflections, recorded at the ambient laboratory temperature of 20 ± 1 °C with graphite-monochromated Mo K$\bar{\alpha}$ radiation (λ 0.710 73 Å), gave the lattice constants $a = 21.618$ (5) Å, $b = 16.870$ (5) Å, and $c = 9.658$ (3) Å. A unit cell content of four $[(C_6H_5)_3PNP(C_6H_5)_3][TcOCl_4]$ moieties gives a calculated density of 1.500 g/cm^3, which is in excellent agreement with the observed density of 1.496 g/cm^3, measured by flotation in a 1,2-dichloroethane/carbon tetrachloride mixture.

Diffraction measurements utilized graphite-monochromated Mo K$\bar{\alpha}$ radiation and the ω-scanning technique with a 4° takeoff angle and a normal-focus X-ray tube. Two Friedel octants of data ($+h,+k,+l$ and $-h,-k,-l$) were collected at a scanning rate of 3°/min for 4350 reflections having $0° < 2\theta_{MoK\alpha} < 43°$, and a single positive octant ($+h,+k,+l$) was collected at 2°/min for reflections having $43° < 2\theta_{MoK\alpha} < 55°$. The scan for each reflection was between ω settings 0.50° above and below its calculated K$\bar{\alpha}$ (λ 0.710 73 Å) doublet value. Counts were accumulated for 19 equal-time intervals during each scan, and those 15 contiguous intervals, which had the highest single accumulated count at their midpoint, were used to calculate the net intensity from scanning. A careful and systematic preliminary study of peak widths (half-height to half-height) indicated little variation from a value of 0.28° for ω for various orientations of the crystal. Background counts, each lasting for one-fourth the total scan time used for the net scan, were measured at ω settings 1.00° above and below the calculated value for each reflection.

A total of 4281 independent positive-octant reflections having $2\theta_{MoK\alpha} < 55°$ (the equivalent of a limiting Cu K$\bar{\alpha}$ sphere) were measured in three concentric shells of increasing 2θ. The six standard reflections, measured every 250 reflections as a monitor for possible disalignment and/or deterioration of the crystal, gave no indication of either. The linear absorption coefficient of the crystal for Mo K$\bar{\alpha}$ radiation[14] is 0.82 mm^{-1}, yielding a μr of 0.25 for the spherical crystal used in data collection. Since the absorption of X-rays by a spherical crystal having $\mu r = 0.25$ is virtually independent of scattering angle,[15] the intensities were reduced without absorption corrections to relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections.

Of the 4281 positive-octant reflections examined, 1068 were eventually rejected as objectively unobserved by applying the rejection criterion, $I < 3\sigma(I)$, where $\sigma(I)$ is the standard deviation in the intensity computed from

$$\sigma^2(I) = C_t + k^2 B$$

C_t being the total count from scanning, k the ratio of scanning time to total background time (in this case, $k = 2$, and B the total background count. The heavy-atom technique, difference Fourier syntheses, and full-matrix least-squares refinement were used with
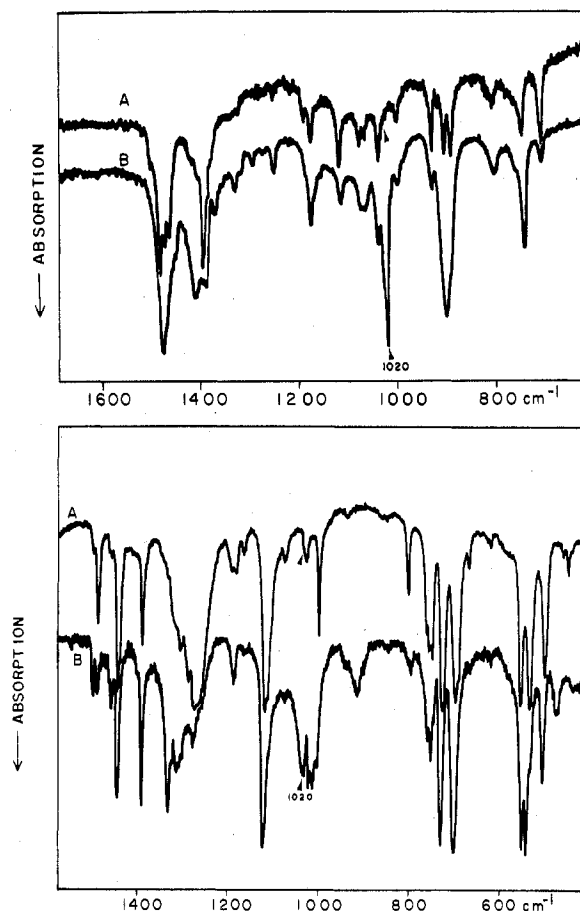

Figure 1. Infrared spectra: top, spectra of (A) (*n*-Bu_4N)Br and (B) (*n*-$Bu_4N)_2[TcOCl_4]$; bottom, spectra of (A) $[(Ph_3P)_2N]Cl$ and (B) $[(Ph_3P)_2N]_2[TcOCl_4]$.

the remaining 3213 independent positive-octant reflections in the determination and refinement of the structure. A Wilson plot and set of normalized structure factors, E_{hkl}, were calculated from these reflections; the various statistical indicators using these normalized structure factors were all in agreement with the choice of a noncentrosymmetric space group.

The atomic coordinates of the technetium atom were readily derived from a Patterson synthesis calculated with the 4350 Friedel pairs having $2\theta_{MoK\alpha} < 43°$. Least-squares refinement of the structural parameters for the Tc atom resulted in a conventional weighted residual

$$R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$$

of 0.411 for 3888 Friedel-pair reflections having $I > 3\sigma(I)$. The inclusion of chlorine atoms, whose positions were selected from the four sets of enantiomeric pairs which appeared in a difference Fourier calculated at this point, reduced R_1 to 0.349 and permitted the proper choice of phosphorus atoms from the two sets of previously equivalent enantiomeric pairs. Unit-weighted isotropic least-squares refinement of the structural parameters for the Tc, four Cl, and two P atoms gave $R_1 = 0.273$ and a conventional weighted residual

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$$

of 0.323 for 3888 Friedel-pair reflections. The remaining 38 non-hydrogen atoms appeared in a difference Fourier synthesis calculated at this point, and isotropic full-matrix least-squares refinement for the 45 nonhydrogen atoms gave $R_1 = 0.075$ and $R_2 = 0.078$. Utilization of anisotropic thermal parameters in further cycles of unit-weighted least-squares minimization of the function $\sum w(|F_o| - K|F_c|)^2$ (where K is the scale factor and w is the weight assigned each reflection) gave $R_1 = 0.044$ and $R_2 = 0.049$ for 3888 Friedel-pair reflections having $2\theta_{MoK\alpha} < 43°$ and $I > 3\sigma(I)$. Atomic positions were then calculated for the 30 phenyl hydrogen atoms by using idealized geometry and a C–H bond length of 0.95 Å. These atomic positions were varied in additional cycles of unit-weighted full-matrix least-squares refinement which converged to $R_1 = 0.027$ and $R_2 = 0.027$ for 3888 Friedel-pair reflections. These and all subsequent structure

Table I. Atomic Coordinates in Crystalline [Ph$_3$PNPPh$_3$] [TcOCl$_4$] ^{a}

atom^b	10^4x	10^4y	10^4z	B_{iso},^{c} A^2	atom^b	10^4x	10^4y	10^4z	B_{iso},^{c} A^2
		Anion					Anion		
Tc	1813.2 (2)	1190.4 (2)	2500.0^d	3.7	Cl$_3$	2008 (1)	556 (1)	4562 (3)	6.8
Cl$_1$	1183 (1)	1063 (1)	606 (2)	5.6	Cl$_4$	2400 (1)	198 (1)	1504 (3)	6.7
Cl$_2$	941 (1)	1683 (1)	3598 (2)	5.9	O	2252 (2)	1958 (2)	2375 (7)	5.7
		Cation					Cation		
P$_1$	4561 (1)	1236 (1)	810 (1)	2.5	C$_{136}$	5748 (2)	1796 (3)	455 (7)	3.7
P$_2$	4000 (1)	2717 (1)	−387 (2)	2.7	C$_{211}$	3812 (2)	3229 (3)	1195 (6)	3.1
N	4315 (2)	1883 (3)	−207 (5)	3.2	C$_{212}$	3202 (3)	3417 (5)	1516 (8)	4.6
C$_{111}$	4403 (2)	1455 (2)	2602 (6)	2.7	C$_{213}$	3078 (3)	3808 (5)	2748 (9)	5.5
C$_{112}$	3776 (2)	1510 (3)	2995 (6)	3.5	C$_{214}$	3547 (4)	4009 (4)	3639 (9)	5.3
C$_{113}$	3632 (3)	1745 (4)	4320 (7)	4.2	C$_{215}$	4156 (4)	3796 (4)	3340 (7)	4.7
C$_{114}$	4096 (3)	1927 (4)	5245 (7)	4.2	C$_{216}$	4284 (3)	3429 (4)	2107 (6)	3.7
C$_{115}$	4706 (3)	1878 (4)	4854 (7)	4.3	C$_{221}$	3300 (2)	2588 (3)	−1380 (6)	3.0
C$_{116}$	4856 (3)	1639 (3)	3522 (6)	3.6	C$_{222}$	3110 (2)	3142 (3)	−2345 (8)	4.0
C$_{121}$	4202 (2)	296 (3)	440 (6)	2.8	C$_{223}$	2592 (3)	2992 (5)	−3148 (8)	4.9
C$_{122}$	3972 (3)	147 (3)	−880 (6)	3.6	C$_{224}$	2268 (3)	2301 (5)	−2987 (8)	4.6
C$_{123}$	3696 (3)	−577 (4)	−1159 (7)	4.2	C$_{225}$	2442 (3)	1756 (4)	−2011 (8)	4.9
C$_{124}$	3652 (3)	−1143 (4)	−155 (8)	4.2	C$_{226}$	2960 (3)	1898 (4)	−1195 (7)	4.0
C$_{125}$	3889 (3)	−1006 (4)	1141 (7)	4.3	C$_{231}$	4513 (2)	3349 (3)	−1352 (6)	3.1
C$_{126}$	4165 (3)	−284 (3)	1448 (7)	3.8	C$_{232}$	4997 (3)	3026 (4)	−2070 (6)	3.7
C$_{131}$	5385 (2)	1119 (3)	562 (5)	2.6	C$_{233}$	5393 (3)	3491 (4)	−2859 (7)	4.7
C$_{132}$	5656 (2)	382 (3)	394 (6)	3.5	C$_{234}$	5283 (4)	4293 (5)	−2929 (8)	5.5
C$_{133}$	6281 (3)	337 (4)	83 (7)	4.1	C$_{235}$	4796 (3)	4625 (4)	−2219 (9)	5.1
C$_{134}$	6630 (3)	1000 (4)	−41 (7)	4.1	C$_{236}$	4411 (3)	4165 (4)	−1419 (8)	4.3
C$_{135}$	6370 (2)	1728 (4)	174 (7)	4.1					

atom^b	10^3x	10^3y	10^3z	B_{iso},^{c} A^2	atom^b	10^3x	10^3y	10^3z	B_{iso},^{c} A^2
H$_{112}$	345 (2)	139 (3)	234 (6)	0 (1)	H$_{212}$	291 (4)	332 (4)	90 (9)	5 (2)
H$_{113}$	313 (3)	184 (4)	467 (10)	5 (2)	H$_{213}$	261 (3)	404 (4)	291 (8)	4 (2)
H$_{114}$	402 (2)	202 (3)	616 (6)	1 (1)	H$_{214}$	348 (3)	424 (4)	434 (8)	4 (2)
H$_{115}$	504 (3)	205 (3)	554 (7)	2 (1)	H$_{215}$	448 (3)	399 (3)	389 (6)	1 (1)
H$_{116}$	526 (2)	168 (3)	321 (6)	1 (1)	H$_{216}$	468 (2)	331 (3)	186 (5)	0 (1)
H$_{122}$	396 (3)	49 (4)	−163 (8)	3 (1)	H$_{222}$	335 (2)	363 (3)	−237 (8)	2 (1)
H$_{123}$	354 (2)	−70 (3)	−196 (6)	1 (1)	H$_{223}$	246 (3)	344 (4)	−371 (8)	4 (2)
H$_{124}$	342 (3)	−169 (3)	−34 (7)	2 (1)	H$_{224}$	197 (3)	230 (3)	−348 (6)	1 (1)
H$_{125}$	381 (3)	−136 (4)	181 (7)	3 (1)	H$_{225}$	222 (3)	122 (4)	−192 (7)	3 (1)
H$_{126}$	435 (2)	−18 (3)	231 (7)	1 (1)	H$_{226}$	311 (2)	155 (3)	−66 (7)	2 (1)
H$_{132}$	541 (3)	−6 (4)	46 (7)	2 (1)	H$_{232}$	508 (3)	257 (3)	−194 (6)	2 (1)
H$_{133}$	648 (3)	−14 (4)	−5 (7)	2 (1)	H$_{233}$	574 (3)	323 (4)	−329 (7)	2 (1)
H$_{134}$	699 (3)	96 (3)	−30 (7)	2 (1)	H$_{234}$	557 (4)	460 (5)	−353 (9)	6 (2)
H$_{135}$	660 (2)	224 (3)	14 (5)	0 (1)	H$_{235}$	477 (2)	513 (3)	−232 (7)	2 (1)
H$_{136}$	552 (3)	231 (3)	61 (7)	2 (1)	H$_{236}$	411 (3)	434 (3)	−89 (7)	2 (1)

^{a} Figures in parentheses are the estimated standard deviations for the last significant digits. ^{b} Atoms are labeled in agreement with Figure 1. ^{c} For nonhydrogen atoms, this is the equivalent isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$ where the β_{ij} are the dimensionless anisotropic temperature factors employed during refinement; for hydrogen atoms, this is the isotropic thermal parameter actually refined. ^{d} This coordinate was held constant and used to fix the unit cell origin; it is therefore listed without an estimated standard deviation.

factor calculations employed anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms, the scattering factors compiled by Cromer and Mann,[16] anomalous dispersion corrections[17] to the scattering factors of Tc, Cl, and P atoms, and a least-squares refinable extinction correction[18] of the form $1/(1 + gI_c)^{1/2}$ (where the extinction coefficient, g, refined to a final value of 4.76×10^{-7}). At this point, the enantiomeric structure (mirrored about $z = 0.25$) was similarly least-squares refined with the Friedel-pair data to give $R_1 = 0.030$ and $R_2 = 0.031$ for 3888 unit-weighted reflections. Since these R value differences clearly indicated the correctness of the initial enantiomeric choice, it was used with the more complete ($2\theta_{MoK\alpha} < 55°$) positive-octant data in all subsequent refinement cycles.

Unit-weighted full-matrix least-squares refinement of the model with anisotropic nonhydrogen atoms and isotropic hydrogen atoms converged to $R_1 = 0.034$ and $R_2 = 0.033$ for 3213 positive-octant reflections having $2\theta_{MoK\alpha} < 55°$ and $I > 3\sigma(I)$. Empirical weights ($w = 1/\sigma^2$) were then calculated from

$$\sigma = \sum_0^3 a_n|F_o|n = 1.06 - 5.41 \times 10^{-3}|F_o| + 8.72 \times 10^{-5}|F_o|^2$$

the a_n being coefficients derived from the least-squares fitting of the curve

$$||F_o| - |F_c|| = \sum_0^3 a_n|F_o|n$$

where the F_c values were calculated from the fully refined model by using unit weights and an $I > 3\sigma(I)$ rejection criterion. The final cycles of full-matrix least-squares refinement utilized these weights with 3213 independent positive-octant reflections to vary the scale factor, the extinction coefficient, and the positional and thermal parameters for 45 anisotropic nonhydrogen atoms and 30 isotropic hydrogen atoms to give final values of 0.033 and 0.037 for R_1 and R_2, respectively.[19] During the final cycle of refinement, no parameter (including those of hydrogen atoms) shifted by more than $0.31\sigma_p$ with the average shift being $0.05\sigma_p$, where σ_p is the estimated standard deviation of the parameter.

The following computer programs were employed in this work with an IBM 360/65 or 370/158 computer: MAGTAPE, SCALEUP, and SCTFT4, data reduction programs written by V. W. Day; FAME, a Wilson plot and normalized structure factor program by R. Dewar and A. Stone; FORDAP, Fourier and Patterson synthesis program, a modified version of A. Zalkin's program; ORFLSE, full-matrix least-squares refinement program, a highly modified version of Busing, Martin, and Levy's original ORFLS; ORFFE, bond lengths and angles with standard deviations by Busing, Martin, and Levy; ORTEP2, thermal ellipsoid plotting program by C. K. Johnson; MPLANE, least-squares mean plane calculation program from L. Dahl's group.

Results and Discussion

Our visual observations on the reduction of the TcO$_4^-$ ion in concentrated HCl with H$_3$PO$_2$ are in agreement with those

Table II. Thermal Parameters for Nonhydrogen Atoms in Crystalline [Ph$_3$PNPPh$_3$] [TcOCl$_4$]^a

| atom^b | anisotropic parameters, A^2 | | | | | | equiv B_{iso},^{c} A^2 |
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	
T				Anion			
Tc	3.14 (1)	3.10 (1)	5.23 (2)	−0.25 (1)	0.02 (2)	−0.18 (2)	3.7
Cl$_1$	6.2 (1)	6.2 (1)	4.8 (1)	0.1 (1)	−0.8 (1)	−0.6 (1)	5.6
Cl$_2$	5.1 (1)	7.6 (1)	6.2 (1)	1.4 (1)	1.0 (1)	−1.4 (1)	5.9
Cl$_3$	7.7 (1)	7.1 (1)	6.9 (1)	0.0 (1)	−2.7 (1)	−1.4 (1)	6.8
Cl$_4$	5.7 (1)	5.6 (1)	11.1 (2)	1.6 (1)	1.0 (1)	−1.9 (1)	6.7
O	5.1 (2)	4.1 (2)	9.8 (4)	−1.2 (2)	−0.4 (3)	0.6 (3)	5.7
				Cation			
P$_1$	2.41 (4)	2.58 (4)	2.44 (4)	0.15 (4)	−0.02 (4)	−0.13 (4)	2.5
P$_2$	2.40 (4)	2.82 (5)	2.89 (5)	0.26 (4)	−0.11 (5)	−0.04 (4)	2.7
N	3.5 (2)	3.5 (2)	2.8 (2)	0.6 (1)	−0.3 (2)	−0.1 (2)	3.2
C$_{111}$	3.1 (2)	2.7 (2)	2.3 (2)	0.1 (1)	−0.1 (2)	−0.2 (2)	2.7
C$_{112}$	3.1 (2)	4.2 (2)	3.3 (2)	−0.2 (2)	0.3 (2)	−0.4 (2)	3.5
C$_{113}$	4.1 (3)	5.0 (3)	3.9 (3)	0.0 (2)	1.3 (2)	−0.3 (2)	4.2
C$_{114}$	6.4 (3)	5.2 (3)	2.6 (2)	0.8 (3)	0.7 (2)	−1.1 (2)	4.2
C$_{115}$	5.3 (3)	5.5 (3)	3.1 (3)	0.4 (3)	−0.5 (2)	−1.3 (2)	4.3
C$_{116}$	3.7 (2)	4.1 (2)	3.1 (2)	0.0 (2)	0.1 (2)	−0.5 (2)	3.6
C$_{121}$	2.8 (2)	2.7 (2)	3.2 (2)	−0.3 (2)	0.5 (2)	−0.5 (2)	2.8
C$_{122}$	3.6 (2)	4.0 (2)	3.5 (2)	−0.6 (2)	−0.3 (2)	−0.7 (2)	3.6
C$_{123}$	3.7 (2)	5.6 (3)	4.6 (3)	−1.3 (2)	0.2 (2)	−2.0 (3)	4.2
C$_{124}$	4.5 (3)	3.9 (3)	6.4 (4)	−1.6 (2)	2.3 (3)	−1.9 (3)	4.2
C$_{125}$	5.4 (3)	3.9 (3)	4.7 (3)	−1.4 (2)	1.6 (3)	−0.6 (2)	4.3
C$_{126}$	4.7 (3)	3.2 (2)	3.7 (3)	−0.4 (2)	0.4 (2)	−0.2 (2)	3.8
C$_{131}$	2.6 (2)	3.0 (2)	2.4 (2)	0.0 (2)	0.1 (2)	−0.4 (2)	2.6
C$_{132}$	2.9 (2)	3.9 (2)	4.1 (3)	0.1 (2)	0.0 (2)	−0.6 (2)	3.5
C$_{133}$	3.5 (2)	4.7 (3)	5.3 (3)	0.8 (2)	−0.2 (2)	−2.0 (3)	4.1
C$_{134}$	2.6 (2)	6.9 (4)	4.3 (3)	0.1 (2)	0.6 (2)	−1.6 (3)	4.1
C$_{135}$	2.7 (2)	5.1 (3)	5.2 (3)	−0.8 (2)	0.5 (2)	−0.2 (3)	4.1
C$_{136}$	3.3 (2)	3.5 (2)	4.3 (3)	−0.4 (2)	0.1 (2)	−0.1 (2)	3.7
C$_{211}$	3.3 (2)	2.8 (2)	3.3 (2)	0.2 (2)	0.6 (2)	−0.2 (2)	3.1
C$_{212}$	3.7 (2)	6.6 (3)	4.4 (3)	1.6 (3)	0.5 (2)	−0.5 (3)	4.6
C$_{213}$	5.1 (3)	7.7 (4)	6.0 (5)	1.8 (3)	2.2 (3)	−1.1 (4)	5.5
C$_{214}$	7.8 (4)	5.1 (3)	4.8 (3)	−0.1 (3)	2.2 (4)	−1.7 (3)	5.3
C$_{215}$	6.1 (3)	5.1 (3)	4.2 (3)	−2.1 (3)	0.7 (3)	−1.2 (3)	4.7
C$_{216}$	3.7 (2)	4.0 (3)	3.6 (3)	−0.6 (2)	0.1 (2)	−0.7 (2)	3.7
C$_{221}$	2.6 (2)	3.6 (2)	3.1 (2)	0.4 (2)	−0.3 (2)	−0.2 (2)	3.0
C$_{222}$	3.5 (2)	4.4 (2)	4.7 (3)	0.0 (2)	−1.1 (3)	0.7 (3)	4.0
C$_{223}$	3.5 (3)	5.9 (3)	6.6 (4)	0.3 (2)	−1.6 (3)	0.9 (3)	4.9
C$_{224}$	2.7 (2)	6.9 (4)	5.7 (4)	0.3 (2)	−1.1 (2)	−1.3 (3)	4.6
C$_{225}$	3.9 (2)	4.9 (3)	6.5 (4)	−0.9 (2)	−0.6 (3)	−0.1 (3)	4.9
C$_{226}$	3.4 (2)	4.3 (2)	4.6 (3)	−0.3 (2)	0.0 (2)	0.6 (2)	4.0
C$_{231}$	3.2 (2)	3.1 (2)	3.2 (2)	−0.2 (2)	−0.5 (2)	0.1 (2)	3.1
C$_{232}$	4.1 (2)	4.0 (2)	3.1 (2)	0.1 (2)	0.2 (2)	−0.2 (2)	3.7
C$_{233}$	4.6 (3)	6.2 (3)	4.1 (3)	−1.0 (3)	1.2 (2)	−0.1 (3)	4.7
C$_{234}$	6.2 (4)	6.4 (4)	5.8 (4)	−2.5 (3)	1.1 (3)	1.3 (3)	5.5
C$_{235}$	6.2 (3)	3.7 (2)	6.7 (4)	−1.4 (2)	−0.1 (3)	1.0 (3)	5.1
C$_{236}$	3.9 (2)	3.9 (2)	5.4 (3)	−0.1 (2)	0.3 (2)	0.0 (2)	4.3

^{a} Figures in parentheses are the estimated standard deviations for the last significant digits. Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; the B_{ij} in A^2 are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. ^{b} Atoms are labeled in agreement with Figure 1. ^{c} Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

recorded in the literature,[2–4,11] namely, that a dark green solution is formed from which, upon the addition of various cations, green solids can be precipitated along with varying amounts of yellow TcCl$_6^-$ salts.

It has been shown that with the tetra-*n*-butylammonium cation a green crystalline solid is obtained, as previously reported.[11] However, we find that this substance has a strong IR absorption at ~1020 cm^{-1}, as shown in Figure 1, for which the only reasonable assignment is to a Tc=O stretching vibration. This is in satisfactory accord with the previous report of ν(Tc=O) bands at lower frequencies for the TcOCl$_5^{2-}$ ion if we assume that we are dealing with a TcOCl$_4^-$ ion, as indicated by the elemental analysis. The introduction of an additional ligand such as Cl$^-$ into a TcOCl$_4^-$ ion in a position trans to the oxygen atom would be expected to weaken the Tc=O bond somewhat and lower its stretching frequency.

We have also found that the *n*-Bu$_4$N$^+$ salt of TcOCl$_4^-$ can be converted into the Ph$_3$PNPPh$_3^+$ salt, which also has a strong infrared band at ca. 1020 cm^{-1}. The identity and complete

structure of [Ph$_3$PNPPh$_3$][TcOCl$_4$] have been determined unequivocally and accurately by X-ray crystallography, as will be reported presently. It may be noted here that the Tc=O distance found, 1.610 (4) Å, is quite short and thus fully consistent with the relatively high value of ν(Tc=O).

Solid-State Structure of [(C$_6$H$_5$)$_3$PNP(C$_6$H$_5$)$_3$][TcOCl$_4$].
The labeling scheme used in the X-ray crystallographic analysis to designate atoms of the oxotetrachlorotechnetate anion and the bis(triphenylphosphin)iminium cation is given in the computer-generated drawings of Figure 2. The final coordinates for all atoms and the anisotropic thermal parameters for the nonhydrogen atoms are given in Tables I and II, respectively. Covalent bond lengths are given in Table III and bond angles for nonhydrogen atoms in Table IV.

Although the gross structural features of the anion and cation could have been predicted from earlier studies, the detailed geometries at Tc and N probably deserve comment. Whereas square-pyramidal TcOCl$_4^-$ would ideally possess C_{4v} symmetry, this anion is somewhat distorted here and possesses

Table III. Covalent Bond Lengths (A) in Crystalline [Ph$_3$PNPPh$_3$] [TcOCl$_4$]^a

Tc-O	1.610 (4)	C$_{221}$-C$_{222}$	1.382 (8)
		C$_{221}$-C$_{226}$	1.389 (8)
Tc-Cl$_1$	2.291 (2)	C$_{222}$-C$_{223}$	1.386 (9)
Tc-Cl$_3$	2.300 (2)	C$_{223}$-C$_{224}$	1.369 (10)
av	2.295 (2, 5, 5)^b	C$_{224}$-C$_{225}$	1.369 (10)
		C$_{225}$-C$_{226}$	1.389 (9)
Tc-Cl$_2$	2.317 (2)	C$_{231}$-C$_{232}$	1.369 (8)
Tc-Cl$_4$	2.310 (2)	C$_{231}$-C$_{236}$	1.396 (8)
av	2.314 (2, 4, 4)	C$_{232}$-C$_{233}$	1.388 (8)
P$_1$-N	1.562 (4)	C$_{233}$-C$_{234}$	1.376 (10)
P$_2$-N	1.572 (4)	C$_{234}$-C$_{235}$	1.374 (11)
av	1.567 (4, 5, 5)	C$_{235}$-C$_{236}$	1.375 (9)
		av	1.380 (9, 10, 31)
P$_1$-C$_{111}$	1.802 (6)		
P$_1$-C$_{121}$	1.800 (5)	C$_{112}$-H$_{112}$	0.97 (5)
P$_1$-C$_{131}$	1.808 (5)	C$_{113}$-H$_{113}$	1.15 (7)
P$_2$-C$_{211}$	1.801 (5)	C$_{114}$-H$_{114}$	0.92 (6)
P$_2$-C$_{221}$	1.804 (5)	C$_{115}$-H$_{115}$	1.03 (6)
P$_2$-C$_{231}$	1.800 (6)	C$_{116}$-H$_{116}$	0.92 (5)
av	1.803 (5, 3, 5)	C$_{122}$-H$_{122}$	0.93 (7)
		C$_{123}$-H$_{123}$	0.87 (6)
C$_{111}$-C$_{112}$	1.411 (7)	C$_{124}$-H$_{124}$	1.07 (6)
C$_{111}$-C$_{116}$	1.359 (7)	C$_{125}$-H$_{125}$	0.89 (7)
C$_{112}$-C$_{113}$	1.376 (8)	C$_{126}$-H$_{126}$	0.94 (6)
C$_{113}$-C$_{114}$	1.379 (9)	C$_{132}$-H$_{132}$	0.91 (6)
C$_{114}$-C$_{115}$	1.374 (9)	C$_{133}$-H$_{133}$	0.93 (6)
C$_{115}$-C$_{116}$	1.386 (8)	C$_{134}$-H$_{134}$	0.83 (6)
C$_{121}$-C$_{122}$	1.392 (8)	C$_{135}$-H$_{135}$	0.99 (5)
C$_{121}$-C$_{126}$	1.383 (8)	C$_{136}$-H$_{136}$	1.01 (6)
C$_{122}$-C$_{123}$	1.386 (8)	C$_{212}$-H$_{212}$	0.88 (8)
C$_{123}$-C$_{124}$	1.364 (10)	C$_{213}$-H$_{213}$	1.10 (7)
C$_{124}$-C$_{125}$	1.371 (10)	C$_{214}$-H$_{214}$	0.79 (7)
C$_{125}$-C$_{126}$	1.389 (8)	C$_{215}$-H$_{215}$	0.94 (5)
C$_{131}$-C$_{132}$	1.384 (7)	C$_{216}$-H$_{216}$	0.91 (5)
C$_{131}$-C$_{136}$	1.391 (7)	C$_{222}$-H$_{222}$	0.97 (5)
C$_{132}$-C$_{133}$	1.388 (8)	C$_{223}$-H$_{223}$	0.97 (7)
C$_{133}$-C$_{134}$	1.354 (9)	C$_{224}$-H$_{224}$	0.80 (6)
C$_{134}$-C$_{135}$	1.368 (9)	C$_{225}$-H$_{225}$	1.04 (6)
C$_{135}$-C$_{136}$	1.375 (8)	C$_{226}$-H$_{226}$	0.85 (6)
C$_{211}$-C$_{212}$	1.392 (8)	C$_{232}$-H$_{232}$	0.80 (6)
C$_{211}$-C$_{216}$	1.389 (8)	C$_{233}$-H$_{233}$	0.96 (6)
C$_{212}$-C$_{213}$	1.387 (11)	C$_{234}$-H$_{234}$	1.00 (9)
C$_{213}$-C$_{214}$	1.371 (12)	C$_{235}$-H$_{235}$	0.87 (5)
C$_{214}$-C$_{215}$	1.396 (11)	C$_{236}$-H$_{235}$	0.87 (6)
C$_{215}$-C$_{216}$	1.370 (9)	av	0.94 (6, 7, 21)

^{a} Figures in parentheses are the estimated standard deviations in the last significant digits. Atoms are labeled in agreement with Figure 1. ^{b} The first number in parentheses following an averaged value of a bond length is the root-mean-square estimated standard deviation of an individual datum; the second and third numbers are the average and maximum deviations from the averaged value, respectively.

Table IV. Bond Angles (deg) for Nonhydrogen Atoms in Crystalline [Ph$_3$PNPPh$_3$] [TcOCl$_4$]^a

OTcCl$_1$	111.5 (2)	P$_2$C$_{221}$C$_{222}$	121.8 (4)
OTcCl$_3$	109.3 (2)	P$_2$C$_{221}$C$_{226}$	118.4 (4)
av	110.4 (2, 11, 11)^b	P$_2$C$_{231}$C$_{232}$	119.8 (4)
OTcCl$_2$	103.0 (2)	P$_2$C$_{231}$C$_{236}$	120.8 (4)
OTcCl$_4$	103.3 (2)	av	120.1 (4, 13, 32)
av	103.2 (2, 2, 2)		
		C$_{116}$C$_{111}$C$_{112}$	120.1 (5)
Cl$_1$TcCl$_2$	85.1 (1)	C$_{111}$C$_{112}$C$_{113}$	119.1 (5)
Cl$_1$TcCl$_4$	85.8 (1)	C$_{112}$C$_{113}$C$_{114}$	120.1 (6)
Cl$_2$TcCl$_3$	85.4 (1)	C$_{113}$C$_{114}$C$_{115}$	120.4 (6)
Cl$_3$TcCl$_4$	85.6 (1)	C$_{114}$C$_{115}$C$_{116}$	119.9 (6)
av	85.5 (1, 2, 4)	C$_{115}$C$_{116}$C$_{111}$	120.3 (5)
		C$_{126}$C$_{121}$C$_{122}$	119.8 (5)
Cl$_1$TcCl$_3$	139.2 (1)	C$_{121}$C$_{122}$C$_{123}$	119.4 (6)
Cl$_2$TcCl$_4$	153.7 (1)	C$_{122}$C$_{123}$C$_{124}$	120.6 (6)
		C$_{123}$C$_{124}$C$_{125}$	120.3 (6)
P$_1$NP$_2$	147.4 (3)	C$_{124}$C$_{125}$C$_{126}$	120.2 (6)
		C$_{125}$C$_{126}$C$_{121}$	119.7 (6)
NP$_1$C$_{111}$	113.3 (2)	C$_{136}$C$_{131}$C$_{132}$	119.4 (5)
NP$_1$C$_{121}$	110.1 (2)	C$_{131}$C$_{132}$C$_{133}$	119.2 (5)
NP$_1$C$_{131}$	109.2 (2)	C$_{132}$C$_{133}$C$_{134}$	121.1 (6)
NP$_2$C$_{211}$	115.6 (2)	C$_{133}$C$_{134}$C$_{135}$	120.0 (5)
NP$_2$C$_{221}$	108.4 (2)	C$_{134}$C$_{135}$C$_{136}$	120.5 (6)
NP$_2$C$_{231}$	108.7 (2)	C$_{135}$C$_{136}$C$_{131}$	120.0 (5)
av	110.9 (2, 24, 47)	C$_{216}$C$_{211}$C$_{212}$	119.9 (6)
		C$_{211}$C$_{212}$C$_{213}$	118.8 (7)
C$_{111}$P$_1$C$_{121}$	106.9 (2)	C$_{212}$C$_{213}$C$_{214}$	120.9 (6)
C$_{111}$P$_1$C$_{131}$	109.6 (2)	C$_{213}$C$_{214}$C$_{215}$	120.2 (7)
C$_{121}$P$_1$C$_{131}$	107.6 (2)	C$_{214}$C$_{215}$C$_{216}$	119.1 (7)
C$_{211}$P$_2$C$_{221}$	108.6 (2)	C$_{215}$C$_{216}$C$_{211}$	120.8 (6)
C$_{211}$P$_2$C$_{231}$	107.1 (2)	C$_{226}$C$_{221}$C$_{222}$	119.7 (5)
C$_{221}$P$_2$C$_{231}$	108.2 (2)	C$_{221}$C$_{222}$C$_{223}$	119.6 (6)
av	108.0 (2, 8, 16)	C$_{222}$C$_{223}$C$_{224}$	120.4 (7)
		C$_{223}$C$_{224}$C$_{225}$	120.6 (6)
P$_1$C$_{111}$C$_{112}$	116.9 (4)	C$_{224}$C$_{225}$C$_{226}$	119.8 (6)
P$_1$C$_{111}$C$_{116}$	122.6 (4)	C$_{225}$C$_{226}$C$_{221}$	119.8 (6)
P$_1$C$_{121}$C$_{122}$	119.7 (4)	C$_{236}$C$_{231}$C$_{232}$	119.3 (5)
P$_1$C$_{121}$C$_{126}$	120.5 (4)	C$_{231}$C$_{232}$C$_{233}$	121.6 (6)
P$_1$C$_{131}$C$_{132}$	122.0 (4)	C$_{232}$C$_{233}$C$_{234}$	118.5 (6)
P$_1$C$_{131}$C$_{136}$	118.5 (4)	C$_{233}$C$_{234}$C$_{235}$	120.6 (6)
P$_2$C$_{211}$C$_{212}$	120.8 (5)	C$_{234}$C$_{235}$C$_{236}$	120.9 (6)
P$_2$C$_{211}$C$_{216}$	119.3 (4)	C$_{235}$C$_{236}$C$_{231}$	119.2 (6)
		av	120.0 (6, 5, 16)

^{a} Figures in parentheses are the estimated standard deviations in the last significant digits. Atoms are labeled in agreement with Figure 1. ^{b} The first number in parentheses following an averaged value of a bond angle is the root-mean-square estimated standard deviation of an individual datum; the second and third numbers are the average and maximum deviations from the averaged value, respectively.

only approximate C_{2v} symmetry with Cl$_1$-Tc-Cl$_3$ and Cl$_2$-Tc-Cl$_4$ angles of 139.2 (1) and 153.7 (1)°, respectively. Although this distortion produces two distinct sets of Tc-Cl bond lengths and O-Tc-Cl bond angles, the average values for these parameters agree well with those previously observed for related MoOCl$_4$L$^-$ compounds.[20] The average Tc-Cl bond length of 2.305 (2, 9, 14, 4) Å[21] here is in agreement with other Tc-Cl bonds when differences in metal oxidation state and coordination number are taken into account. The Tc=O bond length of 1.610 (4) Å is slightly (0.03–0.06 Å) shorter than those recently reported for two other square-pyramidal Tc(V) anionic complexes.[23] Both four-atom groupings which contain Tc, O, and a pair of trans Cl atoms are coplanar to within 0.005 Å, and their least-squares mean planes intersect near the pseudo-C_2 axis in a dihedral angle of 89.9°.

The O···Cl and cis Cl···Cl contacts in the Tc coordination sphere average 3.168 (5, 63, 78, 4) and 3.128 (3, 6, 12, 4) Å, respectively. The Tc atom is displaced by 0.66 Å toward the oxygen from the S_4-ruffled "square base" for four chlorine atoms (average Cl displacement from the four-atom mean plane is 0.14 Å). The average O-Tc-Cl and trans Cl-Tc-Cl

angles of 106.8 (2, 36, 47, 4) and 146.5 (1, 73, 73, 2)° are in close agreement with the corresponding parameters observed for the square-pyramidal MoOCl$_4^-$ anion which possesses crystallographic C_{4v} site symmetry.[20a] Since no interionic contacts here are significantly less than the pertinent sum of van der Waals radii,[24] it is not clear that one may invoke crystal-packing forces as being responisble for the distortion of TcOCl$_4^-$ from idealized C_{4v} symmetry, but, of course, this is possible.

Although a three-atom grouping joined by adjacent double bonds would normally be expected to be linear, the observed P=N=P angle of 147.4 (3) Å is only slightly outside the 137–142° range observed by other workers[25] for this angle in the bis(triphenylphosphin)iminium cation.

The remainder of the structural parameters listed in Tables III and IV are rather unexceptional. The average cationic P=N, P-C, and phenyl C-C bond lengths of 1.567 (4, 5, 5, 2), 1.803 (5, 3, 5, 6), and 1.380 (9, 10, 13, 36) Å are normal values for these bonds and are quite comparable to values observed for this cation in other studies.[25] The 0.94 (6, 7, 21, 30) Å average C-H bond length in the cation is a typical X-ray value for this bond and is in excellent agreement with those
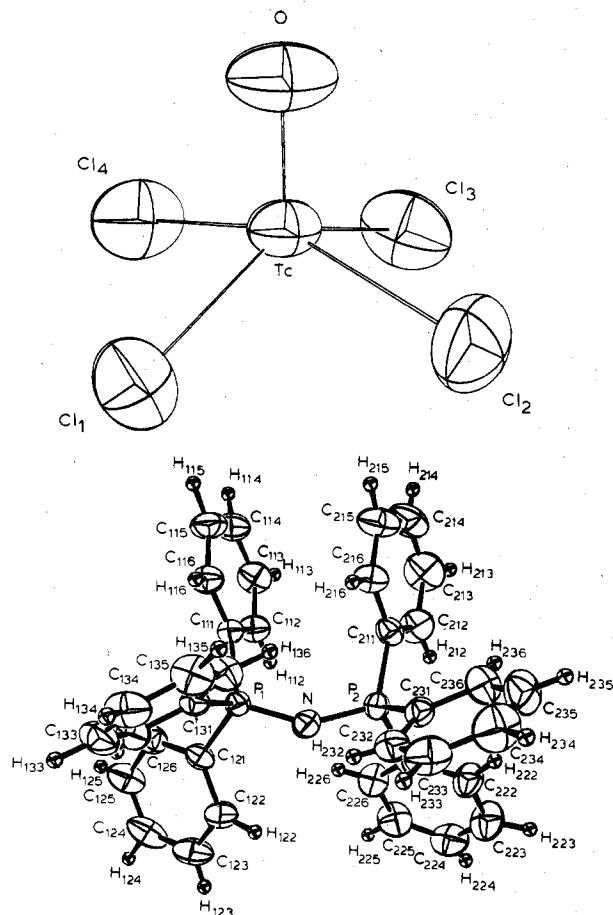
Figure 2. Perspective ORTEP drawings of solid-state structures: (top) the oxotetrachlorotechnetate anion and (bottom) the bis(triphenylphosphin)iminium cation as observed in crystalline [Ph₃PNPPh₃][TcOCl₄]. All nonhydrogen atoms are represented by (50% probability) ellipsoids having the shape, orientation, and relative size consistent with the refined anisotropic thermal parameters. Hydrogen atoms are represented by arbitrarily small spheres for purposes of clarity.

determined by high-precision X-ray studies[26] of other compounds containing similar bonds. The average values of 110.9 (2, 24, 27, 6), 108.0 (2, 8, 16, 6), 120.1 (4, 13, 32, 12), and 120.0 (6, 5, 16, 36)° for the cationic N=P—C, C–P–C, P–C–C, and C–C–C bond angles are also normal values;[25] the average cationic C–C–H angle is 120 (4, 3, 9, 60)°. The bis(triphenylphosphin)iminium cation adopts a cisoidal conformation here, and the atoms of each phenyl group are coplanar to within 0.02 Å.

Concluding Remarks. The results of our research are not surprising in view of the earlier observations of Busey[2] and Jezowska-Trzebiatowska and co-workers.[3,4] Our results simply confirm and extend their observations.

Our work derives its chief significance from the fact that it was undertaken because of the report by Schwochau et al.[11] that H₃PO₂ reduction of TcO₄⁻ in concentrated HCl (exact concentration, or indeed other reaction conditions, not stated precisely) yielded the Tc₂Cl₈²⁻ ion as its *n*-Bu₄N⁺ salt. Our work fails completely to confirm this claim. While it has been shown[9] that Tc₂Cl₈³⁻ can undergo a one-electron oxidation to produce a product with a lifetime in solution of at least 5 min, and we presume that this product is the Tc₂Cl₈²⁻ ion, the only

claim we know of to the actual isolation of this ion in a solid compound is that of Schwochau et al.[11] In view of our findings it appears that further research will be required to find an effective and reproducible method of isolating such a compound.

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