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Synthesis and Characterization of Technetium Complexes with Phosphorus-containing Ligands. The Homoleptic Trimethylphosphite, Dimethylmethylphosphonite and Methyldiethylphosphinite Technetium(I) Cations

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Abstract

Technetium(I) complexes of trimethylphosphite (tmp), dimethylmethylphosphonite (dmmp) and methyldiethylphosphinite (mdep) have been synthesized through direct interaction of the ligand with sodium pertechnetate. The homoleptic, hexakis (ligand), cationic complexes can be isolated as tetraphenylborate salts. Characterization using multinuclear NMR of ^{99}Tc (−422 and −248 ppm *versus* TcO_4^- for the tmp and dmmp complexes, respectively) and ^{31}P (158.5 and 248 ppm *versus* 85% H_3PO_4 for the tmp and dmmp complexes, respectively) gives chemical shift values which compare favorably with previous data on Tc–phosphine and transition-metal–phosphite complexes. Mass spectra (fast atom bombardment and plasma desorption) of the tmp and dmmp complexes exhibit the expected parent peaks and show series of peaks attributed to stepwise loss of ligand molecules or possible decomposition products. X-ray photoelectron spectra of the tmp and dmmp complexes are consistent with formulation as the Tc(I) oxidation state when referenced to well-characterized complexes in known oxidation states.

Introduction

Homoleptic transition-metal–phosphite complexes provide interesting series [1] which bear striking similarity to transition-metal–carbonyl complexes. Aside from limited application to catalysis, these complexes have been studied more for their esoteric qualities than for their practical uses.

Technetium–phosphite complexes are predicted to be mono-cationic for Tc(I) with six ligands. The recent surge in interest toward cationic technetium complexes has been fueled by the discovery of several complexes which accumulate in myocardial tissue [2]. The potential of the title complexes as myocardial scanning agents has prompted us to report fully on the synthesis and characterization of this interesting series of compounds. The trimethylphosphite complex has been reported previously both as a substitution product [3] and as a newly characterized species [1]. The phosphonite and phosphinite complexes are new and when combined with the phosphite complex, comprise the series of complexes which is the subject of this report.

Experimental

Technetium-99 is a long-lived ($t_{1/2} = 2.15 \times 10^5$ yr) isotope which emits a low energy (0.298 MeV) beta particle upon decay. All manipulations with ^{99}Tc were carried out using precautions and safety equipment approved for work with low level radioactivity. Quantities of ^{99}Tc were kept below 100 mg in any single experiment in order to keep exposure to Bremsstrahlung as low as possible.

Sodium pertechnetate was prepared from ammonium pertechnetate (Oak Ridge National Laboratory) by neutralization with sodium hydroxide and was recrystallized from water–ethanol and dried *in vacuo* at 105 °C before use. Trimethylphosphite (Aldrich Chemical Co., Milwaukee, Wis.) was distilled from sodium under argon before use. Solvents were purified and distilled under argon before use. All other chemicals were reagent grade unless otherwise specified.

Synthetic manipulations were carried out under an argon atmosphere using Schlenk techniques or glove bags, unless otherwise specified.

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Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory and the University of California, Berkeley.

Infrared spectra were recorded on a Perkin-Elmer 283B IR Spectrophotometer using polyethylene film as calibrant. Samples were prepared as pressed KBr disks.

Magnetic resonance spectra were obtained using a JEOL FX90Q Fourier transform spectrometer. For ^{99}Tc, a frequency of 20 165 000 Hz, pulse width of 15 μs and an external reference of $NaTcO_4$ in deuterated methanol (*ca.* 0.1 M) were used. For ^{31}P, a frequency of 36 275 300 Hz, a pulse width of 14 μs and an external reference of 85% H_3PO_4 were used. Samples were prepared as solutions in dried deoxygenated solvents and placed in 10 mm tubes with vortex plugs.

Mass spectra were obtained from Schrader Analytical Laboratories (Detroit, Mich.) (fast atom bombardment, FABMS) or at Argonne National Laboratory (^{252}Cf plasma desorption, PDMS). The PDMS were obtained using instrumentation that has been described previously [4]. For the tmp complex, FABMS were obtained from a glycerol matrix; for the dmmp complex, a thioglycerol matrix was used.

X-ray photoelectron spectra were recorded using a Varian IEE-15 spectrometer with a base pressure of 4×10^{-7} torr. The spectrometer was equipped with an Al Kα X-ray source and was operated at a constant pass energy of 100 eV. All spectra were referenced to the 'adventitious' carbon peak at a binding energy of 284.6 eV. Replicate runs produced spectra with binding energies that were reproducible to within ±0.2 eV after referencing to the carbon peak. Samples were mounted by dissolving approximately 0.5 milligrams of the sample in a few drops of methanol (except for *trans*-$TcCl_4(P(C_6H_5)_3)_2$ which was dissolved in CH_2Cl_2). This solution was then uniformly spread onto a clean piece of copper foil and evaporated to dryness. The foil was then mounted on the sample probe and spectra run. TcO_2 was mounted as a powder on cellophane tape.

Hexakis(trimethylphosphite)technetium(I) Tetraphenylborate, $Tc(tmp)_6B(C_6H_5)_4$ (I)

In a typical preparation, sodium pertechnetate (93 mg, 0.5 mmol) was placed in a pressure bottle (0.2 l) with methanol (50 ml) and dissolved. To the resulting solution was added $P(OCH_3)_3$ (12.4 g, 0.1 mol). The pressure bottle was sealed, placed in a water bath at *ca.* 100 °C and heated for 0.5 h. During heating the solution passed through a series of color changes from dark red to orange and finally became yellow, the intensity of the final coloration varying slightly from day to day. Addition of sodium tetraphenylborate (1 M, 10 ml) produced a white precipitate which was collected by filtration and recrystallized from methanol. Yields ranged from 50–75% and could be increased substantially by concentration of the mother liquor and collection of a second and third crop of crystals. *Anal.* Calc. (found) for $TcP_6O_{18}C_{42}H_{74}B$: Tc, 8.51 (7.83); P, 15.99 (15.29, 15.72); C, 43.39 (44.14, 43.40); H, 6.42 (6.66, 6.47)%.

Hexakis(dimethylmethylphosphonite)technetium(I) Tetraphenylborate, $Tc(dmmp)_6B(C_6H_5)_4$ (II)

This complex was prepared in an identical manner to **I** except that dmmp was substituted for tmp. The reaction was judged to proceed at a slower rate as observed by color changes similar to those for **I**. Yields ranged from 40–75%. *Anal.* Calc. (found) for $TcP_6O_{12}C_{42}H_{74}B$: Tc, 9.27 (9.31); P, 17.42 (17.66); C, 47.30 (47.36); H, 6.99 (7.13)%.

Hexakis(methyldiethylphosphinite)technetium(I) Tetraphenylborate, $Tc(mdep)_6B(C_6H_5)_4$ (III)

This complex was prepared in an identical manner to **I** except that mdep was substituted for tmp. The reaction was judged to proceed at a slower rate than for the formation of **II** as observed by color changes similar to those for **I** and **II**. The isolated salt darkened from white to reddish-brown in a few minutes and was not pursued further.

Hexakis(trimethylphosphine)technetium(I) Cation, $Tc(P(CH_3)_3)_6^+$ (IV)

Attempted preparation of this complex in an identical manner to **I** by substituting Me_3P for tmp lead to a final solution which was reddish-brown. The solution contained a number of technetium-containing species as judged by NMR (*vide infra*), among which was **IV**.

Results

Syntheses

The homoleptic cations prepared in this study are readily formed on mixing the pertechnetate salts and the ligand in methanol. The reactions were carried out in a pressure bottle in order to simulate the conditions used in studies of the radiopharmaceutical preparation using tracer amounts of the short-lived ^{99m}Tc. Refluxing methanol at *ca.* 65 °C was equally effective in producing the tmp complex. Also, use of the neat ligands as solvent gave the desired species.

Precipitation of the cations as tetraphenylborate salts produced air-stable crystalline compounds for tmp and dmmp. The mdep complex was crystalline but air-sensitive. Crystal structure studies of the tmp complex are in progress and will be reported elsewhere.

The infrared spectrum of the tmp complex as the tetraphenylborate salt was taken from a pressed KBr pellet. The vibrational frequencies due to the

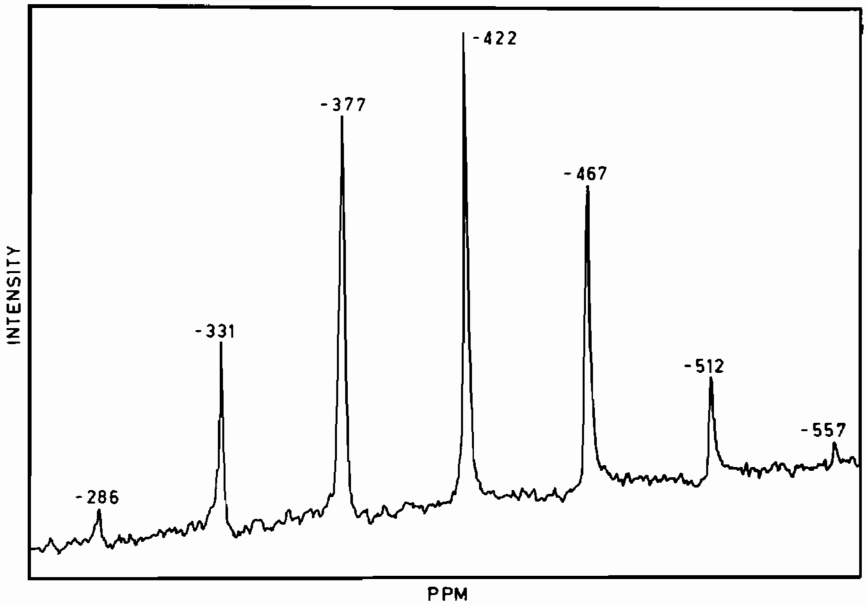

Fig. 1. The ^{99}Tc NMR spectrum of $Tc(tmp)_6^+$ obtained in chloroform-d_1.

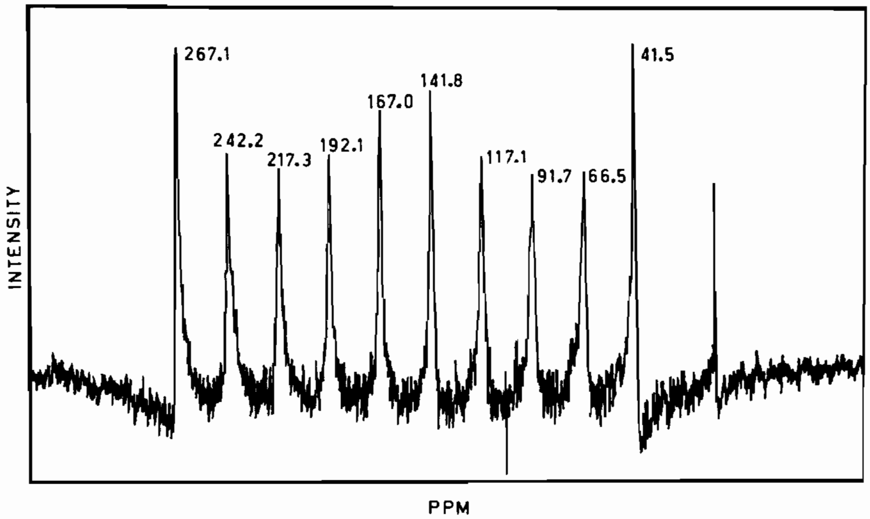

Fig. 2. The ^{31}P NMR spectrum of $Tc(tmp)_6^+$ obtained in methanol-d_4.

P–O bonds shifted to higher energy in the complex (1011 to 1048 and 726 to 762 cm^{-1}), indicating that the tmp was coordinated to Tc. Bands due to $B(C_6H_5)_4^-$ were virtually unchanged from those of $NaB(C_6H_5)_4$, as expected for ionic tetraphenylborate.

Nuclear Magnetic Resonance

Spectra for ^{99}Tc ($I = 9/2$) and ^{31}P ($I = 1/2$) were obtained for I and II. All spectra were taken from solutions in deuterated methanol except for the ^{31}P spectrum of I, which was from a solution in deuterated chloroform. Figures 1 and 2 show the spectra for I. Spectra for II are similar with respect to peak heights and splitting patterns.

The ^{99}Tc spectrum for I consists of a septet centered at −422 ppm *versus* TcO_4^- with a Tc–P coupling constant of 909 Hz. The septet implies that the cation contains six electronically equivalent phosphorus atoms coupled to the Tc. This spectrum is similar to that observed for the $Tc(dmpe)_3^+$ cation (dmpe = 1,2-bis(dimethylphosphino)ethane) [5], where six phosphorus atoms are coordinated to Tc(I). For II, an equivalent septet is observed at −248 ppm with a Tc–P coupling constant of 778 Hz. The chemical shifts of the tmp, dmmp and dmpe complexes (−13 ppm) show an upfield trend as the ligand is varied from phosphite to phosphonite to phosphine, in keeping with the degree of deshielding due to pi-backbonding. For this series, the phosphite is the strongest pi-backbonding ligand and the phosphine the weakest, giving rise to the observed trend. The Tc–P coupling constants also reflect the degree of interaction between the nuclei. For the tmp complex, where significant overlap is expected, the coupling constant is considerably larger than for the dmmp complex. For the dmpe complex, the coupling constant is 574 Hz, expectedly lower than the tmp and dmmp complexes.

Magnetic resonance spectra of the ^{31}P atoms for the tmp, dmmp and dmpe complexes all consist of a decet. The spectrum for **I** is shown in Fig. 2. The decet implies that the phosphorus atoms are electronically equivalent and coupled to one Tc atom ($I = 9/2$). The chemical shifts of the center of the decet are 158.5 ppm for **I** and 248 ppm for **II**. Thus, the trend is the reverse of that seen for the ^{99}Tc chemical shift, as expected. The Tc–P coupling constants observed in the ^{31}P spectra are equivalent to those seen in the ^{99}Tc spectra.

The presence of sharp resonance lines in the magnetic resonance spectra of these complexes is an indication that the complexes are diamagnetic.

Mass Spectra

Fast atom bombardment (FABMS) and plasma desorption (PDMS) mass spectra were obtained for **I**, FABMS only was obtained for **II**. Figure 3 shows the positive ion FABMS of **I**.

For **I**, the positive ion mode was used to produce mass spectra containing a parent peak at 843 mass units (calc. 843.4). The peaks at 719, 595 and 471 m.u. correspond to the loss of one, two and three tmp ligands from the parent ion. In general, the FABMS and PDMS are similar. Differences are noted in the minor peaks. FABMS shows a series of peaks at 829, 815 and 801 m.u., while PDMS detects only the peak at 801 m.u. Another such discrepancy occurs at 705, 691 and 677 m.u. (FABMS) *versus* only 677 m.u. (PDMS). These peaks are suggestive of the loss of fragments of 14 m.u., perhaps corresponding to a CH_2 moiety.

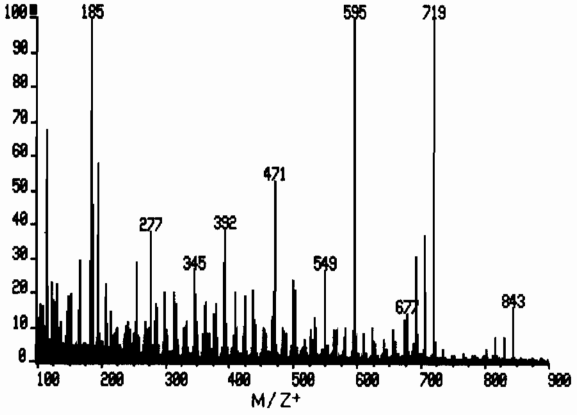

Fig. 3. The FABMS of Tc(tmp)$_6^+$ using a glycerol matrix and positive ion mode.

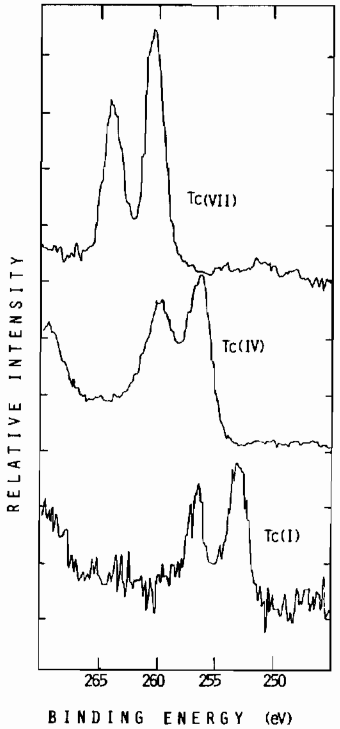

Fig. 4. The X-ray photoelectron spectrum of selected technetium compounds showing binding energies of the Tc(3d) photoelectrons. The Tc(VII), Tc(IV) and Tc(I) represent sodium pertechnetate, ammonium hexachlorotechnetate(IV) and Tc(tmp)$_6$ tetraphenylborate respectively.

For **II**, the FABMS in the positive ion mode shows a parent ion at 747 m.u. (calc. 747.4). Additional peaks at 639, 531 and 421 m.u. are consistent with the successive loss of dmmp ligands. Once again, series of peaks at 733, 625 and 517 m.u. are indicative of the loss of fragments of 14 m.u.

For **I** and **II**, the negative ion FABMS and PDMS (**I** only) shows a strong signal at 318 m.u. which corresponds to the value calculated for the tetraphenylborate ion.

X-ray Photoelectron Spectroscopy (XPS)

Figure 4 illustrates the results of XPS studies of $NaTcO_4$ (Tc(VII)), $(NH_4)_2TcCl_6$ (Tc(IV)), and **I**, (Tc(I)). In each case a doublet was observed for the Tc(3d) electrons ($3d^{5/2,\,3/2}$). A plot of binding energies *versus* oxidation state clearly indicates a linear relation between these properties. The data are consistent with the assignment of an oxidation state of (I) to compound **I**. The binding energy has previously been observed to vary as a function of the formal oxidation state of Tc [6].

Discussion

Syntheses

Synthesis of the homoleptic technetium–tmp cation from pertechnetate and tmp is remarkable for a number of reasons. First of all, the use of the fully oxygenated TcO_4^- species as starting material is an entirely new approach for making binary phosphite–metal complexes. Earlier methods have employed halogen–metal compounds, metal carbonyls, phosphine–metal compounds, metal vapors and π-bonded aryl metal complexes among others. The four oxygen atoms bonded to technetium are removed in the reaction and the $Tc(tmp)_6^+$ cation results. Secondly, the reduction of Tc(VII) to Tc(I), formally a six electron process, represents a much larger reduction of the metal than has previously been required to form the phosphite complex. The aforementioned starting materials are generally already in a low valent state and auxiliary reducing agents often are employed. The use of tmp alone as reducing agent suggests that tmp may be much better at scavenging oxygen from polyoxometallates than has formerly been thought. Interesting possibilities can be envisioned through the reaction of metal oxides with phosphite such as facile methods of synthesis of phosphite–metal complexes. Finally, the use of tmp as solvent insures both a large excess of ligand and an easy separation of the product without the necessity for removal of an inert solvent.

Rates of the reactions, while not quantitatively evaluated, could be inferred relative to one another from the rapidity with which the color changes occurred. The rate with tmp was very fast (~1–5 min for completion) while a decreasing trend in the rates was seen on going from dmmp to mdep to trimethylphosphine. In fact, for trimethylphosphine, a complex mixture of products was formed. This result was interpreted as a lack of sufficient oxygen avidity for trimethylphosphine to drive the reaction to the fully phosphine-substituted product $Tc[P(CH_3)_3]_6^+$. However, another possible explanation may be that the bulky $P(CH_3)_3$ ligand is too sterically demanding to allow the hexakis complex. Evidence for such steric hindrance was seen previously for the Cr–Mo–W group in ultraviolet irradiation experiments of the hexacarbonyls [7]. In these experiments, the maximum number of $P(CH_3)_3$ ligands on the final products were 4(Cr) and 5(Mo, W). Trimethylphosphite showed corresponding values of 5(Cr, W) and 6(Mo). In any case, the π-acidity of the phosphorus ligands does decrease in the order phosphite, phosphonite, phosphinite and phosphine. Assuming that the π-acidity and oxygen avidity are directly related, it is consistent that the rates of reaction occur in the relative order observed.

TABLE I. ^{99}Tc Magnetic Resonance Data

Ligand	Type	Chemical shift[a]	Coupling constant (Hz)[b]
tmp	phosphite	−422	907
dmmp	phosphonite	−248	778
dmpe	phosphine	−13	574

[a] −ppm relative to $^{99}TcO_4^-$. [b] $-J(Tc-P)$.

Nuclear Magnetic Resonance

The ^{99}Tc nucleus is one of the most sensitive to magnetic resonance in the periodic table [8]. Although few studies involving ^{99}Tc magnetic resonance have been reported, the use of this technique is gaining momentum. In this study we have added two data points to the list for chemical shifts and Tc–P coupling constants for Tc(I). When combined with the data for the $Tc(dmpe)_3^+$ cation [5], interesting trends in the data are obvious. The respective chemical shift and coupling constant data are summarized in Table I. Chemical shifts are seen to approach pertechnetate from the low frequency side. The trend in the data lends itself to linear analysis and indeed a nearly linear correlation ($r = -0.995$) is obtained on plotting the chemical shift *versus* the number of oxygen atoms bonded to phosphorus. The amount of shielding of the Tc nucleus is related to the π-donor and π-acceptor ability of the particular ligands. Previous studies with $CpV(CO)_2L_2$ (L = phosphorus ligand) [9, 10] and $Co(NO)_2XL$ (X = halogen, L = phosphorus ligand) [11] have shown similar trends in chemical shift data. In this study, the linear change in chemical shift as a function of number of oxygens on Tc is remarkable. The data clearly reveal the deshielding effect of tmp. The predicted chemical shift for the complex $Tc[(CH_3)_2POCH_3]_6^+$, −139 ppm, can be calculated from the data. Efforts are underway to synthesize the above complex in order to verify this relation.

In the spectrum of the $Tc–P(CH_3)_3$ reaction mixture, a septet of peaks near 0 ppm can be attributed to the existence of the $Tc[P(CH_3)_3]_6^+$ cation. Confirmation of the existence of this cation would be facilitated by the preparation of a pure compound. Comparison of the chemical shift data for the dmpe complex and the $P(CH_3)_3$ complex would provide insight into the effect of a chelating phosphine *versus* a monodentate one.

The coupling constants for the three Tc–P complexes also show a linear relationship as a function of the number of oxygens bonded to phosphorus ($r = 0.998$). The calculated coupling constant for the phosphinite complex is 680 Hz. The coupling constants decrease in the order phosphite, phosphonite, phosphine. While coupling constants generally have not been invoked for consideration of bonding estimates, the existence of π-back-bonding in the Tc–P bond indicates that the coupling constants probably are dominated by orbital and dipolar terms. Such an interpretation is consistent with the data since tmp, the strongest π-back-bonding ligand forms a complex with the largest coupling constant. For **I**, the chemical shift and coupling constant lie at the extreme expected for the strongest complex. **I** is observed to be much more stable than the phosphonite, phosphinite or phosphine complex. The Tc–dmpe complex can be quantitatively oxidized to $Tc(dmpe)_3^{+2}$ at appropriate potentials [5] and it is speculated that oxidative processes are responsible for the instability of the phosphinite and phosphonite complexes. For the $P(CH_3)_3$ complex, we are unable to compare the stability directly with that of the dmpe complex. Such a comparison would be interesting as the chelating dmpe ligands theoretically would be thermodynamically more difficult to remove from the technetium.

The phosphorus magnetic resonance spectra consist of a decet of peaks for both **I** and **II**. The spectra are very similar in form to the spectrum for the $Tc(dmpe)_3^+$ complex [5]. The chemical shifts of the phosphorus resonance are as expected for the greater deshielding of the phosphonite.

Homoleptic phosphite complexes of neighboring second row transition metals have been investigated by ^{31}P magnetic resonance. For $Mo(tmp)_6$, $Ru(tmp)_6^{2+}$ and $Rh(tmp)_6^{3+}$ (172, 126 and 92 ppm, respectively) [12], the chemical shift of the ^{31}P resonance varies linearly as a function of charge. The calculated value for the $Tc(tmp)_6^+$ complex is 155 ppm, in excellent agreement with the observed value. Linear variation of ^{31}P chemical shift as a function of charge has been observed previously for tmp complexes of a different isostructural–isoelectronic series [13]. The data also are interpreted as further evidence of the mono-cationic nature of **I**. Unfortunately, similar correlations are not available for dmmp complexes.

Mass Spectra

Ostensibly, the FABMS and PDMS spectra of **I** and **II** are consistent with the proposed structures. Series of peaks corresponding to the parent ions, TcL_6^+, and to daughter ions formed by successive loss of ligands is observed. However, the series of less intense peaks, e.g., those at 829, 815 and 801 m.u. for **I** are suggestive of an underlying series of compounds which may have implications for a decomposition mode or by-product structure.

For **I**, the mass spectra reveal peaks corresponding to the loss of up to three fragments of 14 m.u. from the parent and the first and second daughter. Formulations of the composition $Tc[P(OCH_3)_3]_{6-n}[POH(OCH_3)_2]_n^+$ (n = 1–3) and $Tc[P(OCH_3)_3]_{5-n}[POH(OCH_3)_2]_n^+$ (n = 1–3) etc., satisfy the observed losses.

Similar structures can be written for **II**, where the $CH_3POH(OCH_3)$ ligand replaces $CH_3P(OCH_3)_2$.

The simplest explanation of the origin of these peaks is the loss of one CH_3 moiety from a tmp ligand and subsequent protonation in the matrix or in the gas phase. With regard to this possibility, it is significant that FABMS, which is done in a protic liquid matrix gives rise to a much larger signal for the series than the PDMS, which is done on a solid film. Previous studies of technetium compounds by FABMS [14, 15] have shown that dealkylation and/or loss of ligand are common fragmentations in FABMS of similar complexes.

Decomposition of phosphites through Michaelis–Arbuzov reactions is well known. The dealkylation reactions of transition-metal–phosphite complexes have been reviewed recently [16]. In general, the reactions lead to the replacement of a $P(OR)_3$ by a $P(O)(OR)_2$ ligand. Among the several mechanisms mentioned, a plausible extension would be the attack of water on a coordinated phosphite to give the $POH(OCH_3)_2$ ligand. Complexes with $POH(OR)_2$ or $PO(OR)_2$ ligands are becoming quite common. Some of the more notable examples are $CpCo[PO(OR)_2]_3$ (($P = C_5H_5$, $R = CH_3$, C_2H_5) [17], $Mn_6(CO)_9[OP(OC_2H_5)_2]_9$ [18] and $PtCl[OP(OCH_3)_2]_2P(C_2H_5)_3$ [19] in which the P–O moiety bridges two metals. Other examples containing discrete ligands or hydrogen bridged ligands are known [20–26]. In addition, complexes of pyrophosphites, formally derived from two $POH(OR)_2$ ligands by condensation and loss of a water molecule are known [19, 27, 28]. The abundance of such complexes lends plausibility to the possible existence of either decomposition products or by-products containing the $POH(OR)_2$ or $CH_3POH(OR)$ ligand. However, the mode of entry of such a compound into the product is not certain. Traces of water in the reaction mixture (possibly as water of crystallization in the $NaTcO_4$) or hydrolysis of the coordinated ligand during work-up are two likely choices. Indeed, the compound $Pt[P(OH)(OCH_3)_2]_2[P(O)(OCH_3)_2]_2$ is synthesized in aqueous solution [21], attesting to the partial hydrolysis which is possible for $P(OCH_3)_3$.

X-ray Photoelectron Spectroscopy (XPS)

The oxidation states of **I** and **II** were determined using XPS. The $Tc(3d^{5/2})$ and $Tc(3p^{3/2})$ peaks were scanned for a series of compounds whose formal oxidation states were known. Since the $Tc(3d^{5/2})$ peak is the most intense, has the narrowest full-width at half-maximum (about 1.8 eV), and has large chemical shifts, it was used to estimate the formal charge on the technetium atom. The $Tc(3p^{3/2})$ peak with a width of about 4 eV was used to confirm our assignment. Table II lists the compounds used and

TABLE II. X-ray Photoelectron Binding Energies of some Technetium Compounds

Compound	Oxidation state	Binding energy (eV)	
		$Tc(3d^{5/2})$	$Tc(3p^{3/2})$
NH_4TcO_4	7+	259.4	432.9
$KTcO_4$	7+	259.3	432.7
$NaTcO_4$	7+	259.5	432.6
$(NH_4)_2TcCl_6$	4+	256.2	429.9
TcO_2	4+	256.6	430.1
trans-$TcCl_4(PO_3)_2$	4+	256.4	430.0
$Tc(tmp)_6^+$	1+	253.2	426.6
$Tc(dmmp)_6^+$	1+	253.4	426.6

the binding energies obtained for both peaks. Note that all three of the Tc^{7+} compounds have binding energies that are identical within the precision of the experiment. The average of those (259.4 eV) was taken to be roughly the binding energy characteristic of Tc^{7+} compounds. Similarly, for the Tc^{4+} compounds very similar binding energies were observed for the peaks of the compounds scanned and the average of 256.4 eV was used for this formal oxidation state. Comparing the binding energies of **I** and **II** with these allowed us to estimate the oxidation state of technetium in these two compounds. Figure 4 shows the $Tc(3d^{5/2}$ and $3d^{3/2})$ spectra for typical Tc^{7+}, Tc^{4+} compounds and **I**. Note that the binding energy for **I** is lower than both Tc^{7+} and Tc^{4+} compounds. By plotting the average binding energy of the standards and extrapolating to the binding energies for **I** and **II**, we estimate that both are in the plus one state.

This is only an approximate method since compounds of the same formal oxidation state often have slightly different binding energies. Only one other paper has appeared in which binding energies of technetium compounds were reported [6]. In this paper the authors reported binding energies of a larger number of technetium compounds. They obtained a range of about 0.9 eV between largest and smallest values for compounds of the same formal oxidation state. From this and noting from the data presented here that there is about a 1 eV shift in binding energy per oxidation state change, our error in the estimation of the oxidation state of these two compounds should be less than ±0.5.

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