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Synthesis and Characterization of Technetiumtetrakis(acetonitrile)bis(triphenylphosphine) Cationic Complexes

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A new route to low-valent technetium complexes containing multiple acetonitrile ligands has been developed. The reduction of $TcCl_4(PPh_3)_2$ with zinc metal dust in acetonitrile results in the formation of $[Tc(CH_3CN)_4(PPh_3)_2][Zn_2Cl_6]_{1/2}$. The hexafluorophosphate salt of the analogous Tc(II) cation can be prepared via chemical oxidation of the Tc(I) species, and the Tc(I) cation can be regenerated via chemical reduction. The compounds have been characterized in the solid state via single-crystal X-ray crystallography, and in solution via a combination of spectroscopic techniques and cyclic voltammetry. The structural parameters found in the two complexes are similar to each other; however, the difference in oxidation state is reflected, as expected, in the spectroscopic results. The electrochemical data, obtained from cyclic voltammograms of $Tc(CH_3CN)_4(PPh_3)_2](PF_6)_n$ ($n = 1,2$), mirror the synthetic results in that both compounds possess a reversible redox couple at –0.55 V versus ferrocene, which has been assigned to the Tc(II)/Tc(I) couple.

Complexes containing acetonitrile ligands are useful precursors for investigating the coordination chemistry of the transition metals.[1] Numerous low-valent technetium coordination compounds have been prepared from the neutral Tc(III) complex $TcCl_3(CH_3CN)(PPh_3)_2$.[2−5] More recently, Cotton et al. have prepared three low-valent cationic technetium complexes containing multiple acetonitrile ligands, $[TcCl_2(CH_3CN)_4](BF_4)$, $[Tc_2(CH_3CN)_{10}](BF_4)_4$, and $[Tc(CH_3CN)_6](BF_4)_2$.[6,7] However, virtually no reactivity studies concerning these interesting compounds have appeared in the literature.[8] This may be due in part to their multistep syntheses via the pertechnetate anion, the ubiquitous starting material for technetium chemistry. In the search for a new route to low-valent technetium complexes containing multiple acetonitrile ligands, the reaction of $TcCl_4(PPh_3)_2$ with zinc was investigated. The neutral Tc(IV) compound is readily accessible in one step from the pertechnetate anion.[9] Whereas the reaction of $TcCl_4(PEt_3)_2$ with zinc in benzene leads to the formation of a metal−metal multiply bonded Tc_2(II,II) complex, $Tc_2Cl_4(PEt_3)_4$,[10] it was rationalized that replacing PEt_3 and benzene with PPh_3 and acetonitrile, respectively, would impede dimerization reactions.

The synthesis of $[Tc(CH_3CN)_4(PPh_3)_2][Zn_2Cl_6]_{1/2}$ and $[Tc(CH_3CN)_4(PPh_3)_2](PF_6)_n$ ($n = 1, 2$) is summarized in Scheme 1. Another example of $[Zn_2Cl_6]^{2-}$ resulting from the reduction of a transition metal complex with zinc is the preparation of $[V_2(THF)_6(\mu\text{-}Cl)_3]^+$ from V(III) chloride.[11] Chemical oxidation of $[Tc(CH_3CN)_4(PPh_3)_2][Zn_2Cl_6]_{1/2}$ with $AgPF_6$ results in isolation of the Tc(II) cation as its hexafluorophosphate salt. The Tc(I) cation can be regenerated as its hexafluorophosphate salt via chemical reduction with cobaltocene. Archer et al. have reported the preparation of $TcCl_3(CH_3CN)(PPh_3)_2$ from $TcCl_4(PPh_3)_2$ using zinc and excess triphenylphosphine in refluxing acetonitrile.[3,4] In the reactions reported herein, the molar ratios of zinc and acetonitrile relative to $TcCl_4(PPh_3)_2$ are larger, and no excess triphenylphosphine is employed. The neutral Tc(III) complex,

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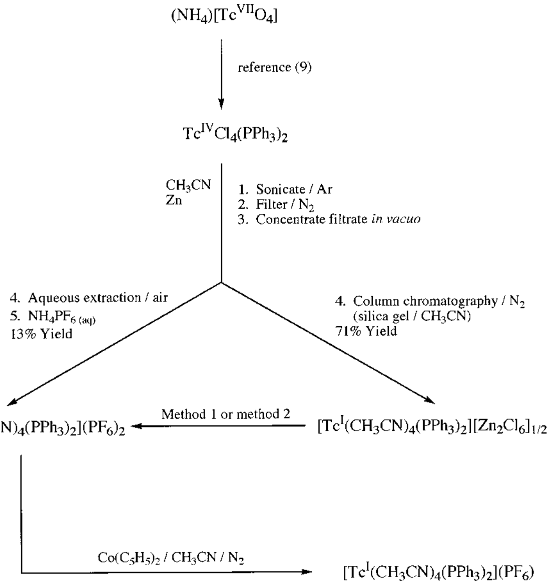
Scheme 1. Synthesis of $[Tc(CH_3CN)_4(PPh_3)_2]^{2+/+}$ Cationic Complexes[a]



[a] Method 1: $AgPF_6/CH_3CN/N_2$/48% yield. Method 2: water/air/NH_4PF_6/36% yield. **CAUTION!** Tc-99 is a weak β^- emitter (E = 0.292 MeV, $t_{1/2} = 2.12 \times 10^5$ years).

$TcCl_3(CH_3CN)(PPh_3)_2$, is only partially soluble in acetonitrile so the larger volume of solvent employed herein may help to keep this potential intermediate in solution. Also, the sonication technique may facilitate the heterogeneous reaction with zinc and $TcCl_4(PPh_3)_2$ or any other technetium species generated in solution during the course of the reaction.

The new compounds are readily soluble in acetonitrile and acetone; however, solutions containing the Tc(I) cation turn from yellow to black over the course of minutes upon exposure to air, whereas pink solutions of the Tc(II) complex are stable toward air over a period of days. Solid samples of the compounds exhibit the same differences in stability upon exposure to air, with the Tc(I) complex turning from yellow to brown over the course of hours and the Tc(II) complex being stable for weeks.

The X-ray crystal structures have been obtained for $[Tc(CH_3CN)_4(PPh_3)_2][Zn_2Cl_6]_{1/2}$[12] and $[Tc(CH_3CN)_4(PPh_3)_2](PF_6)_2{\cdot}2(CH_3)_2CO$.[13] An ORTEP of the Tc(II) cation, which lies on an inversion center, is shown in Figure 1. The structural parameters for the two complexes are very similar to each other. Both cations have a trans arrangement of the phosphine ligands about the metal center, and the four acetonitrile ligands occupy the equatorial plane. A ligand set comprising two phosphorus and four nitrogen donor atoms, regardless of the nature of the N-donor ligand, is rare for technetium coordination chemistry.[14-16] Of the two Tc−P distances found in the Tc(I) complex, the Tc−P(1) distance (2.434(3) Å) is within 3 standard deviations of the Tc−P distance found in the Tc(II) complex (2.4408(14) Å), whereas the Tc−P(2) distance (2.404(3) Å) is slightly shorter. The Tc−P and Tc−N bond distances are in agreement with other structurally characterized Tc(I) and Tc(II) compounds.[14,16] The other bond distances and angles are also unremarkable.

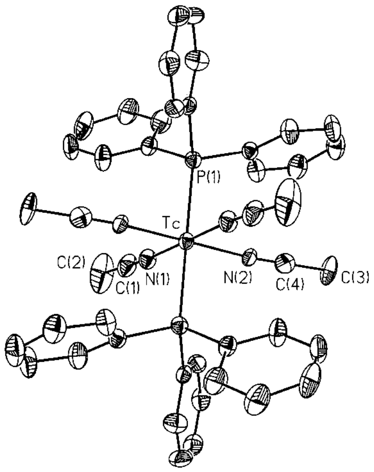


Figure 1. ORTEP diagram of $[Tc(CH_3CN)_4(PPh_3)_2]^{2+}$. Selected bond lengths (Å) and angles (deg): Tc−P(1) 2.4408(14), Tc−N(1) 2.049(5), Tc−N(2) 2.048(5), N(1)−Tc−N(2) 91.54(17), N(1)−Tc−P(1) 89.17(14), N(2)−Tc−P(1) 89.03(13), Tc−N(1)−C(1) 175.7(6), and Tc−N(2)−C(4) 175.4(5).

Whereas the Tc(I) and Tc(II) cations have similar structural parameters, the difference in their oxidation states is reflected, as expected, in their spectroscopic properties.[17,18] The methyl resonance in the ^1H NMR spectrum of the Tc(II) cation is shifted downfield, 1.92 to 3.76 ppm, and is broadened by ca. an order of magnitude relative to the methyl resonance in the ^1H NMR spectrum of the Tc(I) cation. The ^{99}Tc NMR spectrum of the Tc(I) cation consists of a single resonance at +755 ppm. The downfield shift relative to the resonance found in the ^{99}Tc NMR spectrum of $[Tc(CNBu^t)_4(PPh_3)_2]$-

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[12] The data were collected at −90 °C using a Siemens platform goniometer with a CCD detector. The structures were solved by direct methods in conjunction with standard difference Fourier techniques (SHELXTL v5.0, Sheldrick, G. M., and Siemens Industrial Automation, Inc., 1995). Crystal data for $C_{44}H_{42}Cl_3N_4P_2TcZn$: monoclinic, space group = $P2_1/n$, Z = 4, a = 14.593(4) Å, b = 13.922(3) Å, c = 22.152(5) Å, β = 101.412(5)°, V = 4411.6(18) Å^3, ρ_{calcd} = 1.443 g/cm^3, F(000) = 1952. A total of 14060 reflections were collected in the θ range 2.04−20.99° of which 4728 were unique (R_{int} = 0.0962). An empirical absorption correction was applied. The maximum and minimum transmissions were 0.8580 and 0.6751, respectively. The least squares refinement converged normally with residuals of R1 (based on F) = 0.0761, wR2 (based on F^2) = 0.1390, and GOF = 1.157 based on $I > 2\sigma(I)$.

[13] Crystal data for $C_{50}H_{54}F_{12}N_4O_2P_4Tc$: orthorhombic, space group = $Pbca$, Z = 4, a = 16.6859(19) Å, b = 16.5534(18) Å, c = 20.086(2) Å, V = 5547.8(11) Å^3, ρ_{calcd} = 1.428 g/cm^3, F(000) = 2436. A total of 18129 reflections were collected in the θ range 2.01−21.50° of which 3181 were unique (R_{int} = 0.0934). No absorption correction was applied. The least squares refinement converged normally with residuals of R1 (based on F) = 0.0463, wR2 (based on F^2) = 0.1273, and GOF = 1.024 based on $I > 2\sigma(I)$.

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[17] Spectroscopic data for $[Tc(CH_3CN)_4(PPh_3)_2][Zn_2Cl_6]_{1/2}$: ^1H NMR (acetone-d_6) δ 7.58 (m, 12 H, Ph *H*), 7.44 (m, 18 H, Ph *H*), 1.92 (s, 12 H, methyl *H*); ^{99}Tc NMR (acetonitrile-d_3) δ +753 (3300 Hz); ESI(−)MS m/z 170.83 $[ZnCl_3]^-$; UV−vis (CH_3CN) λ_{max} nm (ϵ M^{-1} cm^{-1}) 208 (>50.0 × 10^4); IR (KBr) cm^{-1} 2248.4 (w) ν(C≡N), 2224.6 (s) ν(C≡N).

[18] Spectroscopic and analytical data for $[Tc(CH_3CN)_4(PPh_3)_2](PF_6)_2$: ^1H NMR (acetone-d_6) δ 7.48 (s, 12 H, Ph *H*), 5.79 (s, 18 H, Ph *H*), 3.76 (s, methyl H); ESI(+)MS m/z 932 $\{[Tc(CH_3CN)_4(PPh_3)_2]^{2+}{\cdot}(PF_6)^-\}^+$; ESI(−)MS m/z 145 $(PF_6)^-$; UV−vis (CH_3CN) λ_{max} nm (ϵ M^{-1} cm^{-1}) 206 (>50.0 × 10^4), 254 (>30.0 × 10^4), 532 (100); IR (KBr) cm^{-1} 2264.6 (w) ν(C≡N), 839.0 (s) (PF_6). Anal. Calcd for $C_{44}H_{42}N_4P_4F_{12}Tc$: C, 49.04; H, 3.93; N, 5.20. Found: C, 48.79; H, 3.95; N, 5.14.

(PF_6), −1760 ppm, is consistent with the observation that resonances in ^{99}Tc NMR spectra have been shown to shift downfield with decreasing ligand field strength about the metal center.[19,20] Although magnetic data could not be obtained for the Tc(I) and Tc(II) complexes described herein due to regulatory issues when working with radioactive material, the ^{1}H and ^{99}Tc NMR data are consistent with the expected diamagnetism of a six-coordinate Tc(I) complex and the expected paramagnetism of a six-coordinate Tc(II) complex.

Both compounds have intense bands in the UV region of the spectrum containing shoulders which tail into the visible region. In contrast to the Tc(I) species which does not have any bands in the visible region, the Tc(II) complex has an absorption at 532 nm (100 M^{-1} cm^{-1}). The IR spectra of the Tc(I) and Tc(II) cations display absorptions due to the coordinated acetonitrile ligands. In addition, the Tc(II) complex has a strong band due to the PF_6^- counterion.

The most intense peak in the ESI(+) mass spectrum of $[Tc(CH_3CN)_4(PPh_3)_2](PF_6)_2$, *m*/*z* 932.11, corresponds to the following positively charged moiety which contains one dication and one monoanion, $\{[Tc(CH_3CN)_4(PPh_3)_2]^{2+}\cdot(PF_6)^-\}^+$. At much weaker intensities are peaks corresponding to $[Tc(CH_3CN)_4(PPh_3)_2]^+$ and $[Tc(CH_3CN)_4(PPh_3)_2]^{2+}$, *m*/*z* 787.17 and 393.59, respectively. An ESI(+) mass spectrum of $[Tc(CH_3CN)_4(PPh_3)_2][Zn_2Cl_6]_{1/2}$ was precluded by the air/moisture sensitivity of the cation. However, the ESI(−) mass spectrum displays a peak at *m*/*z* 170.83 which has the proper isotope splitting pattern for $[ZnCl_3]^-$ rather than $[Zn_2Cl_6]^{2-}$. Regardless of whether the $[Zn_2Cl_6]^{2-}$ dianion exists as the mononuclear $[ZnCl_3]^-$ monoanion in solution, or is split under the conditions in the mass spectrometer, the ESI(−) mass spectrum provides spectroscopic evidence, in addition to the crystal structure, for a zinc−chloro anion balancing the positive charge of the $[Tc(CH_3CN)_4(PPh_3)_2]^+$ cation.

The electrochemical data obtained from the cyclic voltammograms of $[Tc(CH_3CN)_4(PPh_3)_2](PF_6)_n$ ($n = 1, 2$) are consistent with the synthetic results. Both cyclic voltammograms reveal a reversible redox couple at −0.55 V, versus an internal ferrocene reference, which has been assigned to the Tc(II)/Tc(I) couple. The cyclic voltammogram of $[Tc(CH_3CN)_4(PPh_3)_2](PF_6)$ has an additional redox couple at −1.3 V, which is the expected potential for the $[Cp_2Co]^+/Cp_2Co$ couple. The preparation of $[Tc(CH_3CN)_4(PPh_3)_2](PF_6)$ from $[Tc(CH_3CN)_4(PPh_3)_2](PF_6)_2$ and cobaltocene also results in $[Cp_2Co](PF_6)$. A comparison of the electrochemical data reveals that $[TcL_4(PPh_3)_2](PF_6)$ is more readily oxidized, by ca. 1.0 V, when L = CH_3CN rather than $CNBu^t$.[20]

Reactivity studies of these new low-valent cationic technetium complexes are currently underway.

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Supporting Information Available: X-ray crystallographic file in CIF format, detailed descriptions of experimental procedures, an ORTEP diagram of $[Tc(CH_3CN)_4(PPh_3)_2]^+$, ^{1}H and ^{99}Tc NMR spectra, ESI mass spectra, and cyclic voltammograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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