

Figure 1. Structure of the $\text{Fe}(\text{SePh})_4^{2-}$ ion with 50% probability ellipsoids shown. Hydrogen atoms are drawn artificially small.

Table IV. Dihedral Angles (deg) and Fe–Se–C Plane–Phenyl Ring Torsion Angles (deg)

| | |
|-----------------------------------|------|
| [Se(1)–Fe–Se(2)]–[Se(3)–Fe–Se(4)] | 84.6 |
| [Se(1)–Fe–Se(3)]–[Se(2)–Fe–Se(4)] | 90.8 |
| [Se(1)–Fe–Se(4)]–[Se(2)–Fe–Se(3)] | 96.3 |
| [Fe–Se(1)–C(1)]–[ring 1] | 16.2 |
| [Fe–Se(2)–C(7)]–[ring 2] | 12.8 |
| [Fe–Se(3)–C(13)]–[ring 3] | 5.2 |
| [Fe–Se(4)–C(19)]–[ring 4] | 9.7 |

and average 2.460 (12) Å; the average Se–C distance is 1.907 (8) Å. The Se–Fe–Se angles range from 103.6 (1) to 114.9 (1)°. The dihedral angles between the perpendicular Se–Fe–Se planes range from 84.6 to 96.3° (Table IV). Coucouvanis et al. proposed that the angular distortions in the MS_4 core result from interactions between the phenyl ortho-protons and the sulfur atoms.³ Since Se would be polarized more easily than S, the chalcogen proton

interaction would be expected to increase. However, the increased length of the Se–C bond over the S–C bond prevents any greater interaction. The average calculated Se...H and Fe...H distances in $[\text{NEt}_4][\text{Fe}(\text{SePh})_4]$ are 3.06 and 3.10 Å, respectively, compared to average S...H and Fe...H distances in $[\text{NEt}_4][\text{Fe}(\text{SPh})_4]$ of 2.96 and 2.99 Å, respectively.³

The FeSe_4 core is slightly less distorted than the CdSe_4 core (Se–Cd–Se angles range from 102.6 (1) to 115.0 (1)°) and significantly less distorted than the ZnSe_4 core (Se–Zn–Se angles range from 98.9 (1) to 119.2 (1)°).¹² In the $[\text{PPh}_4]_2[\text{M}(\text{SPh})_4]$ (M = Fe, Zn) compounds the Fe and Zn structures have similar distortions.³ The differences between the cores in $[\text{NEt}_4][\text{Fe}(\text{SePh})_4]$ and $[\text{NMe}_4][\text{Zn}(\text{SePh})_4]$ may result from a change in packing as a result of the change in cations. Evidence of packing force effects is found in the torsion angles between the M–Se–C planes and their respective phenyl rings. These angles should be 0° owing to π -interactions between the Se lone-pair electrons and the aromatic phenyl ring, but they range from 5.5 to 16.5°.

The differences between the average Fe–S and Fe–Se distances in the $\text{Fe}(\text{QPh})_4^{2-}$ (Q = S, Se) anions is slightly over 0.1 Å. The differences between the average S–C and Se–C bonds is 0.14 Å. In the NEt_4^+ salts the average Fe–Q–C angles are smaller for Q = Se than for Q = S.³ A similar effect is seen for the Zn and Cd species. The higher polarizability of the M–Se bond over the M–S bond is the probable cause of this effect.¹²

Acknowledgment. This research was supported by the National Science Foundation (Grant No. CHE89-22754).

Supplementary Material Available: Complete crystallographic details (Table IS), anisotropic thermal parameters (Table IIS), hydrogen atom positions (Table IIIS), and additional bond lengths and angles (Table VS) for $[\text{NEt}_4]_2[\text{Fe}(\text{SePh})_4] \cdot \text{MeCN}$ (5 pages); structure amplitudes (Table IVS) (21 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Department of Radiology, Harvard Medical School and Brigham and Women's Hospital, Boston, Massachusetts 02115

Synthesis and Characterization of Tetrabutylammonium (2-Aminobenzenethiolato(2-)-S,N)tetrachlorotechnetate(V)

Jessica Cook,[†] William M. Davis,[†] Alan Davison,^{*,†} and Alun G. Jones[‡]

Received October 10, 1990

The reaction of $(n\text{-Bu}_4\text{N})[\text{TcO}(\text{abt})_2]$ (abt = 2-aminobenzenethiolato(2-)-N,S) with 12 M HCl in methanol gives the blue Tc(V) compound $(n\text{-Bu}_4\text{N})[\text{TcCl}_4(\text{abt})]$. Magnetic susceptibility measurements reveal this compound to have two unpaired electrons. This indicates that the ligand, with one hydrogen per nitrogen, is doubly anionic, establishing the metal oxidation state of +5. Infrared data show a single N–H stretching frequency at 3254 cm^{-1} . An X-ray crystal structure of $(n\text{-Bu}_4\text{N})[\text{TcCl}_4(\text{abt})]$ is also reported. Crystal data for $\text{C}_{22}\text{H}_{41}\text{N}_2\text{SCl}_4\text{Tc}$: triclinic, space group $P\bar{1}$ (No. 2), $a = 11.5154$ (8) Å, $b = 13.6200$ (9) Å, $c = 10.5547$ (8) Å, $\alpha = 95.205$ (5)°, $\beta = 116.970$ (7)°, $\gamma = 76.198$ (4)°, and $V = 1432.5$ (4) Å³ to give $Z = 2$ for $D_{\text{calc}} = 1.401$ g/cm³. The structure solution and refinement based on 6893 reflections converged at $R = 0.047$ and $R_w = 0.048$.

Introduction

The technetium(V) oxidation state is dominated by complexes that contain at least one multiply bonded oxygen or nitrogen attached to the Tc(V) center. Many of these technetium–oxygen compounds are formed by the two-electron reduction of per-technetate in the presence of ligands such as thiolates and thio-carboxylates, which tend to stabilize this oxidation state. Others are formed by the protonation of the oxygen and the loss of water to maintain the +5 oxidation state. Only a few Tc(V) compounds, such as TcF_5 , KTcF_6 , and $[\text{Tc}(\text{diars})_2\text{Cl}_4]^+$, do not contain a technetium terminal oxo or a technetium nitrido core.¹

We have obtained a novel Tc(V) complex lacking a $\text{Tc}=\text{O}$ group during our investigations into the chemistry of technetium

with the noninnocent ligand abt [abt = 2-aminobenzenethiolato(2-)-N,S, $(\text{C}_6\text{H}_4\text{NHS}^{2-})$; $\text{Habt} = (\text{C}_6\text{H}_4\text{NH}_2\text{S}^-)$; $\text{H}_2\text{abt} = (\text{C}_6\text{H}_4\text{NH}_2\text{SH}^0)$; $\text{H}_3\text{abt} = (\text{C}_6\text{H}_4\text{NH}_3\text{SH}^+)$]. When the red Tc(V) compound $(n\text{-Bu}_4\text{N})[\text{TcO}(\text{abt})_2]$ is reacted with concentrated HCl in the presence of methanol, the blue complex $(n\text{-Bu}_4\text{N})[\text{TcCl}_4(\text{abt})]$ can be isolated. The extended reaction gives the green complex $(\text{H}_3\text{abt})[\text{TcCl}_6]$ as a minor product. The synthesis and characterization of $(n\text{-Bu}_4\text{N})[\text{TcCl}_4(\text{abt})]$ are described.

Experimental Section

Caution! Technetium-99 is a weak β -emitter ($E = 0.292$ MeV, $t_{1/2} = 2.12 \times 10^5$ years). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere.²

[†] Massachusetts Institute of Technology.

[‡] Harvard Medical School and Brigham and Women's Hospital.

(1) Davison, A.; Jones, A. G. *Int. J. Appl. Radiat. Isot.* 1982, 33, 875.

Table I. Atomic Coordinates for $(n\text{-Bu}_4\text{N})[\text{TcCl}_4(\text{abt})]$

| atom | x | y | z |
|---------|--------------|-------------|--------------|
| Tc | -0.18219 (5) | 0.19047 (4) | -0.03593 (5) |
| Cl(1) | 0.0443 (1) | 0.1709 (1) | 0.03593 (5) |
| Cl(2) | -0.3987 (2) | 0.1905 (1) | -0.2076 (2) |
| Cl(3) | -0.2524 (2) | 0.3161 (1) | 0.0944 (2) |
| Cl(4) | -0.1902 (2) | 0.0479 (1) | 0.0738 (2) |
| S(1) | -0.1665 (2) | 0.3128 (1) | -0.1658 (2) |
| N(1) | -0.1178 (5) | 0.0897 (3) | -0.1715 (5) |
| N(2) | 0.3174 (5) | 0.3234 (4) | 0.0245 (6) |
| C(11) | -0.1568 (5) | 0.2397 (4) | -0.3074 (6) |
| C(12) | -0.1698 (7) | 0.2835 (5) | -0.4272 (7) |
| C(13) | -0.1637 (8) | 0.2259 (7) | -0.5391 (7) |
| C(14) | -0.1411 (8) | 0.1223 (7) | -0.5302 (8) |
| C(15) | -0.1268 (7) | 0.0758 (5) | -0.4103 (7) |
| C(16) | -0.1347 (5) | 0.1346 (4) | -0.2997 (6) |
| C(201) | 0.1779 (6) | 0.3918 (5) | -0.0337 (7) |
| C(202) | 0.1302 (9) | 0.4478 (5) | -0.1700 (8) |
| C(203) | 0.0000 (7) | 0.5253 (5) | -0.2032 (8) |
| C(204) | -0.0549 (8) | 0.5789 (6) | -0.3439 (9) |
| C(205) | 0.4219 (6) | 0.3869 (5) | 0.0804 (7) |
| C(206) | 0.4424 (6) | 0.4418 (5) | 0.2169 (8) |
| C(207) | 0.5371 (7) | 0.5101 (5) | 0.2499 (8) |
| C(208) | 0.5700 (8) | 0.5612 (6) | 0.3910 (8) |
| C(209) | 0.3361 (7) | 0.2586 (5) | -0.0913 (8) |
| C(210) | 0.2391 (8) | 0.1882 (5) | -0.161 (1) |
| C(211) | 0.260 (1) | 0.1297 (7) | -0.279 (1) |
| C(212) | 0.223 (1) | 0.1903 (9) | -0.402 (1) |
| C(213) | 0.3321 (7) | 0.2584 (5) | 0.1441 (8) |
| C(214) | 0.4645 (9) | 0.1839 (6) | 0.214 (1) |
| C(215) | 0.498 (2) | 0.153 (2) | 0.380 (2) |
| C(216) | 0.397 (2) | 0.084 (1) | 0.353 (2) |
| C(215') | 0.460 (2) | 0.105 (1) | 0.304 (2) |
| C(216') | 0.449 (3) | 0.169 (2) | 0.423 (3) |

Ammonium pertechnetate was supplied as a gift by Du Pont/Biomedical Products. Reagents and solvents were used as received. The complex $(n\text{-Bu}_4\text{N})[\text{TcO}(\text{abt})_2]$ was prepared by the method of Bandoli and Gerber.³ The infrared spectrum was recorded on a Mattson Cynus 100 FTIR instrument. The magnetic susceptibility measurements were recorded on a Cahn 7600 Faraday balance. Proton NMR spectra were recorded at 300 MHz on a Varian XL-300 spectrometer. Fast atom bombardment mass spectra (FABMS(+)) and FABMS(-)) were recorded with a JEOL HX110 mass spectrometer operating at ± 10 kV and equipped with a JEOL FAB gun. The JEOL FAB guns produce a beam of 6–8 keV xenon neutrals. The samples were run in a matrix of 3-nitrobenzyl alcohol.

Reaction of $(n\text{-Bu}_4\text{N})[\text{TcO}(\text{abt})_2]$ with Strong Acids. Protonation Studies on $(n\text{-Bu}_4\text{N})[\text{TcO}(\text{abt})_2]$. An ¹H NMR spectrum of $(n\text{-Bu}_4\text{N})[\text{TcO}(\text{abt})_2]$ ³ was obtained by dissolving 4 mg of complex in 1 mL of wet CDCl₃. To show the exchange of the N–H and O–H protons, another ¹H NMR spectrum was obtained after the CDCl₃ solution was equilibrated with D₂O.

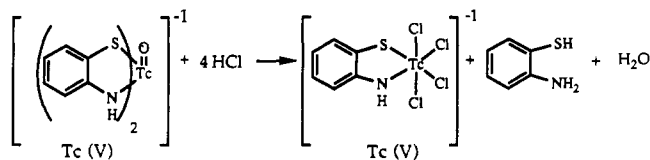
Preparation of $(n\text{-Bu}_4\text{N})[\text{TcCl}_4(\text{abt})]$ (1). To a vigorously stirred mixture of 10 mL of 12 M HCl and 40 mg of $(n\text{-Bu}_4\text{N})[\text{TcO}(\text{abt})_2]$ was added 6 mL of MeOH. After the reaction mixture was stirred for an additional 5 min, any undissolved material was filtered off. The undissolved material was then washed with 2 mL of MeOH, which was added to the reaction flask. The solution was reduced in volume to approximately 2 mL. The dark blue microcrystalline material that precipitated was collected on a fritted disk and dried in vacuo. Yield: 15.5 mg, 39%.

IR (KBr): 3252 (m), 3145 (m), 3114 (m), 3070 (m), 2959 (s), 2931 (m), 2891 (m), 1617 (w), 1547 (m), 1468 (s), 1381 (w), 1141 (m), 755 (m), 432 (w), 387 (m), 342 (s), 329 (m), 318 (s), 299 cm⁻¹ (m). Magnetic susceptibility (room temperature = 25 °C): $\mu_{\text{eff}} = 2.86 \mu_{\text{B}}$.

Preparation of $(\text{H}_3\text{abt})_2[\text{TcCl}_6]$ (2). Dark green crystals of $(\text{H}_3\text{abt})_2[\text{TcCl}_6]$ were obtained by the slow evaporation of the filtrate from the $(n\text{-Bu}_4\text{N})[\text{TcCl}_4(\text{abt})]$ synthesis. Yield: 2.2 mg, 5.5%.

IR (KBr): 3527 (m), 3384 (m), 3186 (m), 3050 (m), 2553 (m), 1982 (m), 1599 (m), 1538 (m), 1472 (m), 1301 (m), 1113 (m), 757 (s), 556 (m), 452 cm⁻¹ (m). FABMS(+): m/z 249 [(Habt)₂H (disulfide)]. FABMS(-): m/z 274 (M – Cl), 239 (M – 2Cl).

Crystallography. A black rod-shaped crystal of $(n\text{-Bu}_4\text{N})[\text{TcCl}_4(\text{abt})]$ was selected from a sample recrystallized from a 4:1 12 M hydrochloric

**Figure 1.** Balanced reaction of $(n\text{-Bu}_4\text{N})[\text{TcO}(\text{abt})_2]$ with HCl.

acid-methanol mixture. The crystal selected measured $0.250 \times 0.250 \times 0.450$ mm. An Enraf-Nonius CAD-4 diffractometer was employed by using the scan mode ω with a maximum 2θ of 54.9° . The octants $+h$, $\pm k$, $\pm l$ were collected, giving a total of 6893 reflections, 6556 of which were unique. The final cycle of refinement was based on 3761 reflections of $I > 3 \sigma(I)$. The technetium atom was located by using direct methods. Neutral scattering factors were used throughout the analysis. An empirical absorption correction was used from the DIFABS/TEXSAN software of the Molecular Structure Corp. The crystal exhibited no significant decay under X-ray irradiation. The non-hydrogen atoms were refined anisotropically, and their atomic parameters are listed in Table I.

The position of the nitrogen-bound hydrogen atom was initially determined from a difference Fourier map. The positional and thermal parameters were optimized over three subsequent least-squares calculations. In the final cycles of refinement this hydrogen atom was held fixed as were all other hydrogen atoms whose positions were calculated: $B_{\text{eq}}(\text{H}) = 1.2B_{\text{eq}}(\text{C})$, $\langle d_{\text{C-H}} \rangle = 0.95 \text{ \AA}$.

Disorder was located in one *n*-butyl group of the tetra-*n*-butylammonium counterion. The disorder is confined to the ultimate and penultimate carbon atoms of the group (C(215) and C(216)). The disorder was clearly visible in difference Fourier maps as being a 2-fold site anomaly. The disorder was modeled with equal occupancy for each participating atom.

Results and Discussion

The reaction of $(n\text{-Bu}_4\text{N})[\text{TcO}(\text{abt})_2]$ with concentrated HCl in MeOH produces the blue species $(n\text{-Bu}_4\text{N})[\text{TcCl}_4(\text{abt})]$ (Figure 1). If this reaction mixture is heated and allowed to stand over night, the green complex $(\text{H}_3\text{abt})_2[\text{TcCl}_6]$ is formed in low yield. This was confirmed by an X-ray crystallographic structural determination on $(\text{H}_3\text{abt})_2[\text{TcCl}_6]$.⁴ Presumably the synthesis of $(n\text{-Bu}_4\text{N})[\text{TcCl}_4(\text{abt})]$ proceeds via the protonation of the oxygen atom in $(n\text{-Bu}_4\text{N})[\text{TcO}(\text{abt})_2]$, which is subsequently lost as water.

Bandoli et al. report the technetium–oxygen bond length for $(n\text{-Bu}_4\text{N})[\text{TcO}(\text{abt})_2]$ as 1.73 (2) Å, which is 0.07 Å longer than previously reported values for technetium(V)–oxo species containing a single Tc=O group.³ This abnormally long bond appears to render the oxygen susceptible to protic attack, as evident from the ¹H NMR data. In wet CDCl₃ the oxygen becomes protonated and the neutral Tc(V) species is formed, establishing an equilibrium between the anionic and neutral species. The O–H proton at 7.74 ppm integrates less than 1:2:8 with respect to the N–H and aromatic protons. If the sample is saturated with H₂O prior to when a spectrum is obtained, the integration of the O–H proton is close to that anticipated. As expected, vigorously washing the NMR sample with D₂O prior to obtaining a spectrum causes the N–H and O–H hydrogens to be replaced with deuterium. This is confirmed by the absence of a signal at 7.74 ppm (O–H) and 8.42 ppm (N–H) in the NMR spectrum.

The IR spectrum of $(n\text{-Bu}_4\text{N})[\text{TcCl}_4(\text{abt})]$ confirms the absence of the Tc=O moiety with no absorption in the established 890–1020-cm⁻¹ region.⁵ A single N–H absorption occurs at 3252 cm⁻¹, which is consistent with a single N–H proton. The Tc–N and Tc–S bands occur at 432 and 387 cm⁻¹, respectively. In $(\text{H}_3\text{abt})_2[\text{TcCl}_6]$, the N–H bands occur at higher wavenumbers (3527 and 3385 cm⁻¹) due to the uncoordinated nature of the H₃abt. The S–H stretching band appears at 2553 cm⁻¹. These data support the $(\text{H}_3\text{abt})_2^+$ identity of the counterion.

The FAB(+) mass spectrum of $(\text{H}_3\text{abt})_2[\text{TcCl}_6]$ displays a peak at m/z 249, which corresponds to the disulfide species $(\text{Habt})_2\text{H}^+$, which presumably results from the oxidation of $(\text{H}_3\text{abt})_2^{2+}$ in the matrix. The negative ion FAB(–) mass spectrum has peaks at

(2) Davison, A.; Orvig, C.; Trop, H. S.; Sohn, M.; DePamphilis, B.; Jones, A. G. *Inorg. Chem.* **1980**, *19*, 1988.

(3) Bandoli, G.; Gerber, T. I. *Inorg. Chim. Acta* **1987**, *126*, 205.

(4) Davison, A.; Davis, W.; Cook, J. Unpublished results.

(5) Mazzi, U. *Polyhedron* **1989**, *8*, 1683.

Table II. Selected Bond Lengths (Å) and Angles (deg) for (n-Bu₄N)[TcCl₄(abt)]

| | | | |
|----------------|-----------|----------------|------------|
| Tc-N(1) | 2.145 (4) | Tc-Cl(3) | 2.322 (2) |
| Tc-S(1) | 2.322 (2) | Tc-Cl(4) | 2.390 (2) |
| Tc-Cl(1) | 2.361 (2) | N(1)-H(1) | 0.943 |
| Tc-Cl(2) | 2.324 (2) | | |
| N(1)-Tc-Cl(3) | 172.7 (1) | Cl(3)-Tc-Cl(4) | 98.01 (6) |
| N(1)-Tc-Cl(2) | 86.3 (1) | Cl(2)-Tc-S(1) | 90.89 (6) |
| N(1)-Tc-S(1) | 82.3 (1) | Cl(2)-Tc-Cl(1) | 173.42 (6) |
| N(1)-Tc-Cl(1) | 88.3 (1) | Cl(2)-Tc-Cl(4) | 87.95 (6) |
| N(1)-Tc-Cl(4) | 89.2 (1) | S(1)-Tc-Cl(1) | 92.01 (6) |
| Cl(3)-Tc-Cl(2) | 93.41 (6) | S(1)-Tc-Cl(4) | 171.55 (6) |
| Cl(3)-Tc-S(1) | 90.41 (6) | Cl(1)-Tc-Cl(4) | 88.31 (6) |
| Cl(3)-Tc-Cl(1) | 92.48 (6) | | |

Table III. X-ray Data for the Structure Determination of (n-Bu₄N)[TcCl₄(abt)]

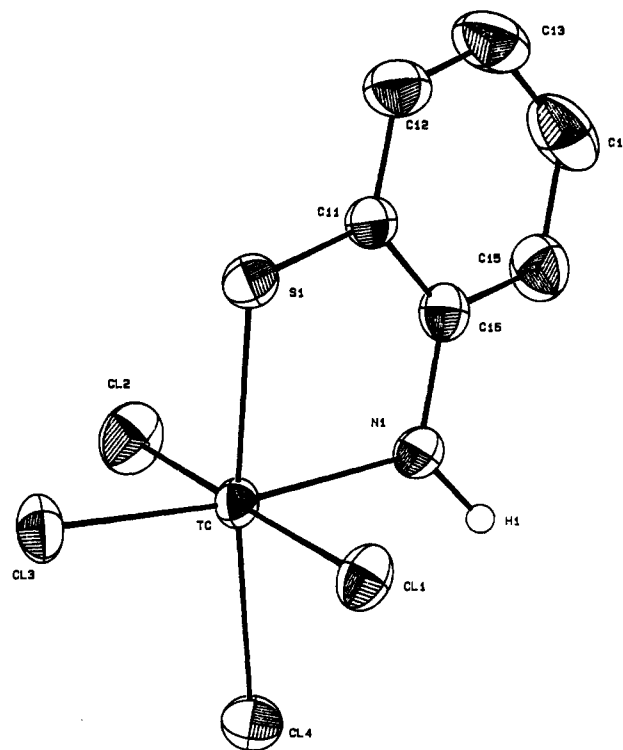
| | |
|--|---|
| C ₂₂ H ₄₁ N ₂ SCl ₄ Tc | fw = 604.45 |
| a = 11.5154 (8) Å | space group = P $\bar{1}$ (No. 2) |
| b = 13.6200 (9) Å | T = 23 °C |
| c = 10.5547 (8) Å | λ = 0.71069 Å (graphite monochromated) |
| α = 95.205 (5)° | ρ_{calcd} = 1.401 g/cm ³ |
| β = 116.907 (7)° | μ = 9.40 cm ⁻¹ |
| γ = 76.198 (4)° | R = 0.047, R _w = 0.048 |
| V = 1432.4 (4) Å ³ | GOOF = 1.28 |
| Z = 2 | |

m/z 274 and 239 corresponding to TcCl₅⁻ and TcCl₄⁻, respectively, both of which display the expected chlorine isotope splitting patterns.

In solution (n-Bu₄N)[TcCl₄(abt)] undergoes a rapid color change at room temperature. In the absence of air and at low temperature this compound is stable for an extended period of time. The UV spectra, as well as mass spectrometry results, were obtained, but they were deemed unreliable due to the color change observed whenever (n-Bu₄N)[TcCl₄(abt)] is in solution. In solvents such as CH₂Cl₂, CHCl₃, THF, and MeOH decomposition seems to occur, whereas in strongly coordinating solvents such as pyridine a color change to deep orange occurs suggesting the coordination of the solvent and the formation of a new complex.

The degree of protonation of the nitrogen atom in 2-aminobenzenethiolate can greatly affect this ligand's chemical properties when bound to metals. When there is a single N-H proton as in Ni(abt)₂, the ligand behaves similarly to dithiolenes.⁶ However, when the amine group retains both protons as is the case in Pt(II)- and Pd(II)-Habt complexes, the ligand does not display dithiolenic character.⁷⁻⁹ This ability of 2-aminobenzenethiol to be bound as a mono- or dianion renders the oxidation state of the transition metal ambiguous unless the number of N-H protons on the complex is known with certainty. Magnetic susceptibility measurements were obtained at room temperature (25 °C) on a Faraday balance to determine whether the technetium was in the +4 or +5 oxidation state. The complex (n-Bu₄N)[TcCl₄(abt)] was found to have a μ_{eff} = 2.86 μ_{B} , which corresponds to two unpaired electrons and unambiguously establishes that the Tc is in the +5 oxidation state with an abt²⁻ and not an Habt⁻ ligand.

Due to the difficulties associated with the reactive nature of this compound, X-ray diffraction was employed to further characterize the complex. Atomic coordinates for complex I are listed in Table I, and the selected bond lengths and angles are listed in Table II. The experimental details for the data collection are listed in Table III. The molecule shows distorted octahedral geometry imposed primarily by the 82.3 (1)° bite angle of the abt ligand. An ORTEP diagram of (n-Bu₄N)[TcCl₄(abt)] is shown in Figure 2. Although the Tc-Cl bond lengths determined for

**Figure 2.** ORTEP diagram showing the molecular structure of (n-Bu₄N)[TcCl₄(abt)] with 35% probability ellipsoids.**Table IV.** Least-Squares Plane Determination

| atom | dist, Å | esd, Å |
|-------|------------------------------|--------|
| | Plane No. 1 ^a | |
| Tc | 0.0023 | 0.0005 |
| Cl(4) | -0.0114 | 0.0018 |
| Cl(3) | -0.0031 | 0.0017 |
| S(1) | -0.0107 | 0.0017 |
| N(1) | -0.0132 | 0.0049 |
| | Atoms Outside of Plane No. 1 | |
| H(1) | 0.2886 | |
| Cl(1) | 2.3597 | |
| Cl(2) | -2.3171 | |

^a Mean deviation from plane = 0.0081 Å; χ^2 = 103.7.

Cl(2) and Cl(3), Tc-Cl(2) = 2.324 (2) Å and Tc-Cl(3) = 2.322 (2) Å, are longer than the 2.309 (2) Å reported for the Tc(V) complex (AsPh₄)[TcOCl₄], they are comparable to the 2.322 (1)-Å distance reported for the nitrido analogue (AsPh₄)[TcNCl₄].¹⁰ All four of the Tc-Cl bond lengths in (n-Bu₄N)[TcCl₄(abt)] are shorter than the average Tc-Cl distance of 2.442 (4) Å in the eight-coordinate Tc(V) species [TcCl₄(diars)₂]⁺.¹¹ The longest of the four reported Tc-Cl bonds occurs in the chloride ligand located trans to the sulfur bond. This is expected, since in octahedral complexes thiolato ligands have been noted to exhibit a trans structural effect.¹² The mutually trans chloride ligands show significant differences in Tc-Cl bond lengths, Tc-Cl(1) = 2.361 (2) Å versus Tc-Cl(2) = 2.324 (2) Å. This difference in bond length is attributed to the nonbonded interaction between Cl(1) and H(1). According to the least-squares plane determination (see Table IV), H(1) lies on the same side of the plane as Cl(1) and the distance between these two atoms is 2.561 Å. This gives a distance of 0.339 Å less than the sum of the van der Waals radii of hydrogen and chlorine, implying a repulsion between the two atoms and resulting in the lengthening of the Tc-Cl(1) bond.

- Larkworthy, L. F.; Murphy, J. M.; Phillips, D. J. *Inorg. Chem.* **1968**, *7*, 1437.
- Gardner, J. K.; Pariyadath, N.; Corbin, J. L.; Stiefel, E. I. *Inorg. Chem.* **1978**, *17*, 897.
- Stiefel, E. I.; Waters, H. J.; Billig, E.; Gray, H. B. *J. Am. Chem. Soc.* **1965**, *87*, 3016.
- Balch, A. L.; Rohrscheid, F.; Holm, R. H. *J. Am. Chem. Soc.* **1965**, *87*, 2301.

- Baldas, J.; Colmanet, S. F. *Aust. J. Chem.* **1989**, *42*, 1155.
- Glavin, K.; Whittle, R.; Johnson, J. F.; Elder, R. C.; Deutsch, E. J. *Am. Chem. Soc.* **1980**, *102*, 2103.
- Elder, R. C.; Florian, L. R.; Lake, R. E.; Yacynych, A. M. *Inorg. Chem.* **1973**, *12*, 2690.

The Tc-N(1) bond length of 2.145 (4) Å in (*n*-Bu₄N)-[TcCl₄(abt)] indicates less multiple-bond character than is displayed in either the octahedral complex Tc^{VI}(abt)₃¹³ or the square-pyramidal complex (*n*-Bu₄N)[TcO(abt)₂]₃,³ where the average Tc-N distances are 1.995 (11) and 2.08 (2) Å, respectively. This Tc^V-N bond length of 2.145 (4) Å is in good agreement with the average single-bond Tc-N distance of 2.125 (11) Å reported for the complex [Tc(cyclam)O₂]⁺.¹⁴ The Tc-S distance is reported to be 2.322 (2) Å. This value falls within the range of values reported for Tc^V square-pyramidal complexes and a Tc^{VI} octahedral abt complex. For the Tc^V complex (*n*-

Bu₄N)[TcO(abt)₂]₃ the average value of 2.30 (1) Å is reported, and a distance of 2.35 (10) Å is reported for the Tc^{VI} complex Tc^{VI}(abt)₃.¹³

Acknowledgment. We express our appreciation to Dr. Michael Clarke for his assistance with the magnetic susceptibility measurements. Mass spectral data were provided by the MIT Mass Spectrometry Facility, which is supported by NIH Grant No. RR00317 (to K. Biemann). This research was supported in part by USPHS Grant No. 5 R01 CA 34970 and DOE Grant No. DE-FG02-87ER60526.

Supplementary Material Available: Tables SI-SV, listing respectively complete X-ray data, atomic positional parameters including hydrogens and isotropic thermal parameters, anisotropic thermal parameters, intramolecular atomic distances, and intramolecular bond angles (13 pages); Table SVI, listing calculated and observed structure factors (26 pages). Ordering information is given on any current masthead page.

(13) Baldas, J.; Boas, J.; Bonnyman, J.; Mackay, M. F.; Williams, G. A. *Aust. J. Chem.* **1982**, *35*, 2413.

(14) Volkert, R. A.; Holmes, D.; Van Derveer, G.; Barefield, E. K. *Inorg. Chem.* **1981**, *20*, 2386.

Contribution from the Department of Chemistry,
The Pennsylvania State University, University Park, Pennsylvania 16802

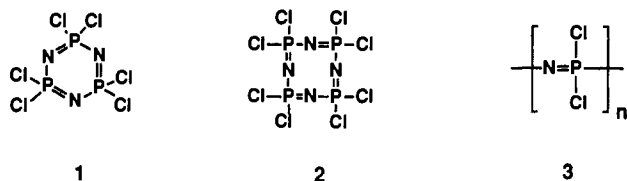
Synthesis of Cyclic Phosphazenes with Isothiocyanato, Thiourethane, and Thiourea Side Groups: X-ray Crystal Structure of N₃P₃(NMe₂)₃(NCS)₃

Harry R. Allcock,* J. Steven Rutt, and Masood Parvez

Received August 28, 1990

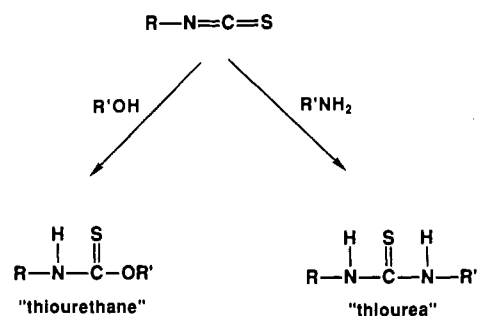
Reaction of the cyclic trimeric phosphazene [NP(NCS)₂]₃ with alcohols, ROH (R = CH₃, C₂H₅, 1-C₃H₇, 1-C₄H₉, and 2-C₃H₇), in THF resulted in the formation of thiourethane derivatives, [NP(NHCSOR)₂]₃, via a nongeminal reaction pathway. Reactions of [NP(NCS)₂]₃ with amines, RNH₂ (R = H, CH₃, C₆H₅, 1-C₄H₉, and 1-C₈H₁₇), in THF yielded thiourea derivatives, [NP(NHCSNR)₂]₃. Interaction of the cyclic tetramer [NP(NCS)₂]₄ with alcohols and amines also yielded thiourethane and thiourea derivatives, although the reactivity of the tetramer was lower than that of the trimer. The reactivity of the isothiocyanato groups was influenced by the steric and electronic effects of cosubstituent side groups such as trifluoroethoxy or dimethylamino. X-ray crystallographic analysis of *cis*-nongeminal-[NP(NMe₂)(NCS)]₃ was carried out, and the structure was compared with those of [NP(NCS)₂]₃ and [NP(NCS)₂]₄. *cis*-nongeminal-[NP(NMe₂)(NCS)]₃ crystallized in the triclinic space group *P* $\bar{1}$. Unit cell parameters were *a* = 8.377 (7) Å, *b* = 9.030 (3) Å, *c* = 14.093 (7) Å, α = 85.55 (3)°, β = 74.91 (5)°, γ = 83.96 (4)°. The final *R* and *R*_w values were 0.047 and 0.074. The reactions of the cyclic phosphazenes served as models for those of the analogous macromolecular phosphazenes.

Cyclic and high-polymeric phosphazenes have been prepared that bear a wide variety of organic, organometallic, and inorganic side groups.¹⁻⁴ Hexachlorocyclotriphosphazene (**1**) and the cyclic tetrameric analogue **2** undergo a ring-opening polymerization when heated at 250 °C to form poly(dichlorophosphazene) (**3**), and the chloro units of species **1-3** can be replaced by organic side groups via nucleophilic replacement reactions.



Small molecule phosphazenes such as **1** or **2** serve as small molecule models for the development of similar chemistry at the high-polymeric level.⁵ Furthermore, X-ray diffraction studies of cyclic trimeric and tetrameric phosphazene species can provide clues to the electronic structure of the high polymers.⁶ Mech-

Scheme I



anistic studies are more easily carried out with small-molecule species.

The focus of this paper is on the chemistry of cyclic phosphazene compounds that bear isothiocyanato side groups.^{7,8} Isothiocyanates (R-NCS) have the ability to undergo addition reactions with alcohols and amines to form thiourethanes and thioureas (Scheme I). Thiourethane and thiourea linkages are characterized by hindered rotation about the C-N bonds caused by resonance effects.⁹ Little is known about the properties of cyclic or high-

- (1) Allcock, H. R. *Chem. Eng. News* **1985**, *63* (11), 22.
 (2) Allcock, H. R. *Phosphorous-Nitrogen Compounds*; Academic: New York, 1972.
 (3) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541.
 (4) Allen, C. W. In *Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic: London, 1987.
 (5) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.
 (6) Craig, D. P.; Paddock, N. L. In *Nonbenzenoid Aromatics*; Snyder, J. P., Ed.; Academic: New York, 1971.

- (7) Patai, S., Ed. *The Chemistry of Cyanates and Their Thio Derivatives*; John Wiley: Chichester, England, 1977.
 (8) Newmann, A. A., Ed. *Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives*; Academic: London, 1975.
 (9) Walter, W.; Reubke, K. J. In *The Chemistry of Amides*; Zabicky, J., Ed.; Interscience: London, 1970.