

Experimental Section

Ammonium [⁹⁹Tc]pertechnetate (58 mg mL⁻¹ in 0.1 mol L⁻¹ NH₄OH solution) was obtained from Amersham International plc. Infrared spectra were determined for KBr disks on a Perkin-Elmer 197 spectrophotometer. Microanalyses were performed by the Australian Micro-analytical Service, Melbourne.

Cesium Pentachloronitridotechnetate(VI). Ammonium pertechnetate (58 mg, 0.32 mmol) was mixed with concentrated HCl (36% w/w, 20 mL), and then NaN₃ (200 mg, 3.1 mmol dissolved in 0.5 mL of water) was carefully added to the mixture. The mixture was heated under reflux for 15 min and the orange-red solution allowed to cool. HCl was removed in a rotary evaporator and the residue extracted with 2 × 5 mL of CH₃CN to leave a residue of colorless inorganic salts. The orange-red acetonitrile solution was evaporated to dryness and the residue dissolved in 4 mL of concentrated HCl. Addition of CsCl (250 mg in 0.5 mL of water) gave a red-brown precipitate, which was collected by filtration, washed with a little concentrated HCl, and dried under vacuum. Yield: 144 mg (81% based on Tc). Mp: >360 °C. Anal. Calcd for Cl₅Cs₂N₂Tc: Cl, 31.9; N, 2.52. Found: Cl, 32.2; N, 2.26. IR (KBr): only one peak at 1027 cm⁻¹ due to Tc≡N.

Tetraphenylarsonium Tetrabromonitridotechnetate(VI). AsPh₄[TcNCl₄] (50 mg, 0.08 mmol) was dissolved in the minimum amount of acetone and then added to 5 mL of acetone containing 1.25 g of dissolved anhydrous LiBr. The mixture rapidly turned a deep blue and was heated under reflux for 5 min. Acetone was removed in a rotary evaporator, and the residue was extracted with 2 × 5 mL of dry CH₂Cl₂. The deep blue CH₂Cl₂ extract was evaporated to dryness and the residue recrystallized from acetonitrile to give deep blue crystals of AsPh₄[TcNBr₄] (52 mg, 81% yield). Mp: 291–293 °C dec (lit.⁹ 293–295 °C dec). IR: ν_{max} 1482 s, 1439 s, 1436 vs, 1085 vs, 1074 s (Tc≡N), 977 s, 742 vs, 688 vs, 680 vs cm⁻¹.

Dichlorobis(triphenylphosphine)nitridotechnetium(V). AsPh₄[TcNCl₄] (50 mg, 0.08 mmol) was dissolved in 5 mL of CH₃CN, and to this solution was added PPh₃ (125 mg, 0.54 mmol) in 5 mL of CH₃CN. Pink-tan crystals precipitated from the mixture and were collected by filtration, washed with CH₃CN, and dried (50 mg, 90% yield based on Tc). Mp: 231–232 °C (lit.⁵ 227 °C). IR: ν_{max} 1480 vs, 1433 vs, 1094 vs, 1088 vs (Tc≡N), 750 s, 742 vs, 707 s, 690 vs cm⁻¹.

Tetraethylammonium Tetrakis(isothiocyanato)(acetonitrile)nitridotechnetate(V). Ammonium pertechnetate (58 mg, 0.32 mmol) was reacted with HCl and NaN₃ and the acetonitrile extract prepared as described in the preparation of Cs₂[TcNCl₄]. The acetonitrile extract (3 mL) was added to a solution of KNCS (350 mg, 3.6 mmol) in 10 mL of water. A number of color changes occurred, and the mixture became orange-brown. Addition of NEt₄Br (170 mg, 0.81 mmol) to the mixture gave an orange-brown precipitate, which was collected by filtration and recrystallized from acetonitrile to give red-brown crystals (114 mg, 55% yield based on Tc). Mp: commences softening with decomposition at 160 °C. Anal. Calcd for C₂₂H₄₃N₅S₄Tc: C, 40.86; H, 6.70; N, 17.33; S, 19.83. Found: C, 41.28; H, 6.83; N, 17.45; S, 19.8. IR: ν_{max} 2300 vw, 2272 vw, 2110 vs, 2085 vs, 1482 s, 1442 m, 1170 m, 1081 m (Tc≡N), 998 m, 828 w, 785 m cm⁻¹.

Bis(diethylthiocarbamate)nitridotechnetium(V). Na[S₂CNEt₂] (200 mg, 1.2 mmol) was slowly added to the acetonitrile extract (25 mL) prepared from 58 mg of NH₄TcO₄. The solution was heated, which resulted in darkening and the formation of a brownish precipitate. The mixture was taken to dryness in a rotary evaporator and the residue extracted with 20 mL of CH₂Cl₂. The dark brown extract was transferred to a silica chromatography column (2.5 × 4 cm) from which a yellow solution was eluted by CH₂Cl₂. Yellow crystals that deposited on concentration of the solution were collected by filtration. Yield: 74% based on Tc. Mp: 254–256 °C (lit.⁴ 253–254 °C dec). IR: ν_{max} 1512 vs, 1438 s, 1284 s, 1205 s, 1070 vs cm⁻¹.

Bis(8-quinolinethiolato)nitridotechnetium(V). The acetonitrile extract (10 mL) prepared from 58 mg of NH₄TcO₄ was added dropwise to a solution of 250 mg of 8-quinolinethiol hydrochloride (1.26 mmol) in 50 mL of CH₃CN. A brown precipitate formed, which was collected by filtration and washed with diethyl ether. The brown precipitate was dissolved in CH₂Cl₂-C₆H₆ (1:1 v/v) and placed on a silica chromatography column (1 × 10 cm). A yellow-orange solution was eluted from the column with the same solvent and concentrated. The orange crystalline precipitate that formed was collected by filtration, washed with diethyl ether, and dried. Yield: 41% based on Tc. Mp: 286–289 °C dec. Anal. Calcd for C₁₈H₁₂N₂S₂Tc: C, 49.89; H, 2.79; N, 9.70; S, 14.8. Found: C, 49.0; H, 2.10; N, 9.36; S, 12.8. IR: ν_{max} 1494 vs, 1454 m, 1367 m, 1299 s, 1212 m, 1064 s, 1000 s, 821 vs, 774 vs, 690 s cm⁻¹.

Table I. Atomic Positional Coordinates, with Esd Values in Parentheses, for [TcN(C₉H₆NS)₂]

atom	x	y	z
Tc	0.0	0.13784 (3)	0.25
S(1)	-0.13747 (5)	0.25897 (13)	0.24867 (5)
N(1)	0.0380 (1)	0.1832 (3)	0.3966 (2)
N(2)	0.0	-0.0831 (5)	0.25
C(1)	0.1199 (2)	0.1401 (4)	0.4560 (2)
C(2)	0.1457 (2)	0.1568 (4)	0.5530 (2)
C(3)	0.0856 (2)	0.2213 (4)	0.5902 (2)
C(4)	-0.0028 (2)	0.2688 (4)	0.5302 (2)
C(5)	-0.0696 (2)	0.3363 (4)	0.5634 (2)
C(6)	-0.1539 (2)	0.3753 (4)	0.5012 (3)
C(7)	-0.1760 (2)	0.3500 (4)	0.4049 (3)
C(8)	-0.1127 (2)	0.2882 (4)	0.3693 (2)
C(9)	-0.0248 (2)	0.2463 (3)	0.4325 (2)
H(1)	0.162 (2)	0.100 (5)	0.425 (2)
H(2)	0.203 (6)	0.064 (9)	0.592 (5)
H(3)	0.094 (3)	0.239 (7)	0.655 (3)
H(5)	-0.068 (4)	0.351 (7)	0.620 (4)
H(6)	-0.204 (3)	0.405 (5)	0.525 (3)
H(7)	-0.228 (3)	0.375 (4)	0.367 (3)

Crystallography. Single crystals of bis(8-quinolinethiolato)nitridotechnetium(V) suitable for X-ray diffraction studies were grown by slow evaporation at room temperature of a CH₂Cl₂ solution. The crystal chosen for data collection was examined by oscillation and Weissenberg photography, and the space group was determined as either C2/c or Cc from the photographs and the systematic absences identified during data collection. Unit cell parameters were derived by a least-squares analysis¹¹ of the setting angles, determined on a diffractometer at 21.5 °C with Cu Kα radiation (λ = 1.5418 Å), for 10 reflections well separated in reciprocal space and each with 2θ greater than 40°.

Crystal Data: C₁₈H₁₂N₂S₂Tc, M_r = 433.34, monoclinic, a = 15.92 (1) Å, b = 7.347 (6) Å, c = 15.33 (2) Å, β = 110.89 (8)°, V = 1675.2 Å³, Z = 4, D_c = 1.72 Mg m⁻³, space group C2/c, μ(Cu Kα) = 8.982 mm⁻¹.¹²

Intensity data were recorded at 21 ± 1 °C on an automatic Siemens AED diffractometer with nickel-filtered Cu Kα radiation. The crystal had well-developed faces of type (111), (100), and (001) with perpendicular distances between faces of 0.25, 0.20, and 0.25 mm, respectively. The crystal was aligned with the 1, 1, 1 axis approximately parallel to the diffractometer φ axis. Intensities were measured by the "five-values" θ-2θ scan procedure detailed by Hoppe,¹³ with a 2θ scan rate of 10° min⁻¹. A reference reflection, monitored every 20 reflections, showed no significant variation in intensity during data collection. A hemisphere of data (3369 reflections) was collected within the limit (sin θ)/λ ≤ 0.61 Å⁻¹. After equivalent reflections were combined, all 1618 unique data were used for the structure refinement, with negative intensities set to zero. Integrated intensities were corrected for Lorentz and polarization effects and for absorption.¹²

Structure Solution and Refinement. The structure was solved by the heavy-atom method. Since the Tc atom lay on a twofold rotation axis, the alternative space group Cc was rejected, and the successful refinement of the structure confirmed the choice of C2/c as the correct space group. Fourier-difference syntheses yielded the positions of all other atoms. The scattering model included anisotropic thermal parameters for all non-hydrogen atoms, variable positional coordinates and individual isotropic thermal parameters for hydrogen atoms, and an empirical isotropic extinction parameter.¹³ Full-matrix least-squares refinement (135 variables) converged with R = 0.029, R_w = 0.041, and χ = 3.66.¹⁵ The maximum parameter shift-to-error ratio for non-hydrogen atoms at convergence was 0.4:1. The largest peaks on a final difference synthesis were of heights 0.55 and -0.59 e Å⁻³.

Final atomic positional coordinates, with esd's in parentheses, are listed in Table I. Neutral-atom scattering-factor curves for C, N, and S were from ref 16, that for Tc was from ref 17, and that for H from ref 18.

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- R_w = [Σw(ΔF)²/ΣwF_o²]^{1/2} and χ = [Σw(ΔF)²/(N_o - N_v)]^{1/2} where ΔF = |F_o| - |F_c| and N_o and N_v are the numbers of observations and variables, respectively.
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Real and imaginary anomalous-dispersion corrections were applied to the non-hydrogen atoms.¹² Structure determination and refinement were performed with the SHELX 76 program system¹⁴ on the Commonwealth Department of Health IBM 3083J computer.

Results and Discussion

Reactions of the TcNCl_4^- Anion. A general method for the preparation of technetium complexes in solution is by the reduction of the $\text{Tc}^{\text{VII}}\text{O}_4^-$ ion in the presence of coordinating ligands. This method may, however, result in the formation of a mixture of products.¹⁹ The alternative method of ligand substitution of a reduced technetium species has largely relied on the two readily available starting materials, $\text{Tc}^{\text{V}}\text{OX}_4^-$ ($\text{X} = \text{Cl}, \text{Br}$) and TcX_6^{2-} ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). Ligand substitution reactions of these species have been used to prepare a variety of Tc^{V} and Tc^{IV} complexes.²⁰

We have recently shown that the reaction of TcO_4^- with an excess of NaN_3 in concentrated HCl produces an orange-red solution from which $\text{N-}i\text{-Bu}_4[\text{TcNCl}_4]$ or $\text{AsPh}_4[\text{TcNCl}_4]$ may be precipitated in high yield by the addition of the organic cations.⁹ These salts are readily soluble in acetonitrile, which provides a convenient medium for reaction with organic ligands. Alternatively, the hydrochloric acid reaction mixture may be evaporated to dryness, and extraction with acetonitrile gives an orange solution free of the colorless inorganic salts produced in the reaction. The acetonitrile extract may be used to react with ligands directly. Evaporation of the acetonitrile extract to dryness and redissolution in concentrated HCl result in an orange solution from which $\text{AsPh}_4[\text{TcNCl}_4]$ may be quantitatively precipitated by addition of AsPh_4Cl .

The addition of CsCl to the salt-free HCl solution described above results in the precipitation of red-brown crystals of six-coordinate $\text{Cs}_2[\text{TcNCl}_5]$. The additional chloride ligand trans to the nitrido group results in the lowering of the $\text{Tc}\equiv\text{N}$ IR absorption in $\text{Cs}_2[\text{TcNCl}_5]$ to 1027 cm^{-1} compared to 1076 cm^{-1} in five-coordinate $\text{AsPh}_4[\text{TcNCl}_4]$. The precipitation of MOX_4^- and MNX_4^- salts by large cations and of MOX_5^{2-} and MNX_5^{2-} salts by small cations and the lowering of the $\text{M}=\text{O}$ or $\text{M}\equiv\text{N}$ IR frequency in the six-coordinated species is characteristic of transition-metal oxo- and nitrido-halo complexes.^{21,22}

The chloro ligands in TcNCl_4^- are labile. Addition of $\text{AsPh}_4[\text{TcNCl}_4]$ to lithium bromide in acetone results in the rapid formation of deep blue $\text{AsPh}_4[\text{TcNBr}_4]$, which we have previously prepared directly by the reaction of TcO_4^- and NaN_3 in concentrated HBr . The $\text{AsPh}_4[\text{TcNCl}_4]$ and $\text{Cs}_2[\text{TcNCl}_5]$ salts are stable in air but are readily hydrolyzed by water. Addition of water to an acetonitrile solution of $\text{AsPh}_4[\text{TcNCl}_4]$ or dissolution of $\text{Cs}_2[\text{TcNCl}_5]$ in water results in a violet-purple solution, the color of which slowly fades with the formation of a brown gelatinous precipitate. The structure of this precipitate has not been determined, but it is clear that the $\text{Tc}\equiv\text{N}$ group is retained as shown by the IR absorption at 1058 cm^{-1} . Also, the precipitate is soluble in concentrated HCl to give an orange solution from which $\text{AsPh}_4[\text{TcNCl}_4]$ may be precipitated by the addition of AsPh_4Cl . The stability of the $\text{Tc}\equiv\text{N}$ bond to aqueous hydrolysis is surprising and indicates the utility of TcNCl_4^- as a source of $\text{Tc}\equiv\text{N}$ complexes in aqueous solution. It may be noted that while OsO_3N^- is stable, $\text{MoO}_3\text{N}^{3-}$ and $\text{ReO}_3\text{N}^{2-}$ have been reported to be instantly hydrolyzed by water to form ammonia.³

The reaction of TcNCl_4^- with an excess of the reducing ligands PPh_3 , $[\text{S}_2\text{CNET}_2]^-$, NCS^- , and 8-quinolinethiol (thiooxine) results in the reduction of Tc^{VI} to Tc^{V} . Thus, the reaction of PPh_3 with $\text{AsPh}_4[\text{TcNCl}_4]$ in acetonitrile yields $[\text{TcNCl}_2(\text{PPh}_3)_2]$ and the

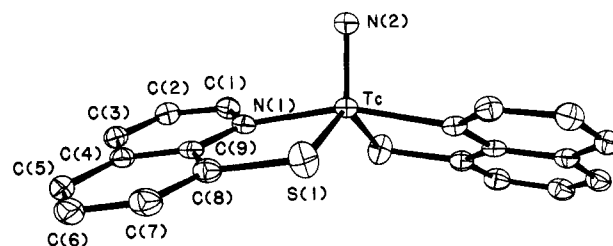


Figure 1. ORTEP drawing of the $[\text{TcN}(\text{C}_9\text{H}_6\text{NS})_2]$ molecule. The thermal ellipsoids are drawn at the 30% level.

reaction of the acetonitrile extract of the $\text{TcO}_4^-/\text{NaN}_3/\text{HCl}$ reaction mixture with $\text{Na}[\text{S}_2\text{CNET}_2]$ or 8-quinolinethiol yields $[\text{TcN}(\text{S}_2\text{CNET}_2)_2]$ or $[\text{TcN}(\text{C}_9\text{H}_6\text{NS})_2]$, respectively. It may be noted that the reaction of TcOCl_4^- with 8-quinolinol has been reported to give the six-coordinate complex $[\text{TcO}(\text{C}_9\text{H}_6\text{NS})_2\text{Cl}]$.²³ Here the $\text{Tc}^{\text{V}}\text{OCl}_2^{2+}$ "core", compared to the $\text{Tc}^{\text{V}}\text{N}^{2+}$ "core" in $[\text{TcN}(\text{C}_9\text{H}_6\text{NS})_2]$, is required to give a neutral species. Reaction of the acetonitrile extract with an aqueous solution of KNCS results in a number of color changes to finally give an orange-brown solution. Addition of NEt_4Br and recrystallization of the precipitate formed from acetonitrile gives $[\text{NEt}_4]_2[\text{TcN}(\text{NCS})_4(\text{CH}_3\text{CN})]$.

The structure of $[\text{TcN}(\text{C}_9\text{H}_6\text{NS})_2]$ has been established by X-ray diffraction, and the structure of $[\text{NEt}_4]_2[\text{TcN}(\text{NCS})_4(\text{CH}_3\text{CN})]$ is based on the microanalytical data, the IR absorption peaks at 1081 ($\text{Tc}\equiv\text{N}$), 2085 , and 2110 (NCS) cm^{-1} , and two very weak IR peaks at 2272 and 2300 cm^{-1} attributable to the coordinated acetonitrile ligand. Very weak $\text{C}\equiv\text{N}$ absorptions in the solid-state IR spectra of acetonitrile complexes have been noted for $[\text{TcN}(\text{NCS})_2(\text{PPh}_3)_2(\text{CH}_3\text{CN})]$ ⁶ and for a series of $[\text{ReX}_3(\text{RCN})(\text{PPh}_3)_2]$ ($\text{R} = \text{alkyl}; \text{X} = \text{Cl}, \text{Br}$) complexes.²⁴ The $[\text{TcN}(\text{S}_2\text{CNET}_2)_2]$ and $[\text{TcNCl}_2(\text{PPh}_3)_2]$ complexes were identical with the compounds prepared by the literature methods.^{4,5}

The ready reduction of the $\text{Tc}^{\text{VI}}\text{N}^{3+}$ core to the more stable $\text{Tc}^{\text{V}}\text{N}^{2+}$ core is not unexpected and parallels the behavior of the TcO system where complexes containing the $\text{Tc}^{\text{VO}}\text{O}^{3+}$ core are common and stable. Tc^{VI} compounds are uncommon, and TcNX_4^- ($\text{X} = \text{Cl}, \text{Br}$) and TcO_4^{2-} are the only Tc^{VI} ions to have been prepared in solution. The $[\text{NMe}_4]_2[\text{TcO}_4]$ salt is, however, reported to be extremely sensitive to oxygen and atmospheric moisture, which cause rapid oxidation and disproportionation.²⁵ As is expected from the position of rhenium in the periodic table, the ReNCl_4^- ion appears to be less readily reduced than TcNCl_4^- . Thus, while reaction of TcNCl_4^- with NCS^- results in reduction of Tc^{VI} to Tc^{V} , the reaction of $\text{AsPh}_4[\text{ReNCl}_4]$ with NCS^- has been reported to give $[\text{AsPh}_4]_2[\text{Re}^{\text{VI}}\text{N}(\text{NCS})_5]$.²⁶

The TcNCl_4^- ion appears to strongly favor substitution by "soft" rather than by "hard" ligands. Since "soft" ligands such as phosphines or thiols are also reducing ligands, this means that the TcNCl_4^- ion is useful as a source of $\text{Tc}^{\text{V}}\equiv\text{N}$ rather than $\text{Tc}^{\text{V}}\equiv\text{N}$ compounds. As a source of $\text{Tc}^{\text{V}}\equiv\text{N}$ complexes, TcNCl_4^- is still the agent of choice, since it is easy to prepare and appears to be a more versatile intermediate than $[\text{TcNCl}_2(\text{PPh}_3)_2]$. Thus, while reaction of NCS^- with $[\text{TcNCl}_2(\text{PPh}_3)_2]$ results in substitution of only the chloride ligands to give $[\text{TcN}(\text{NCS})_2(\text{PPh}_3)_2]$,⁶ the reaction of NCS^- with TcNCl_4^- results in fully substituted $[\text{TcN}(\text{NCS})_4(\text{CH}_3\text{CN})]^{2-}$.

Crystal Structure of Bis(8-quinolinethiolato)nitridotechnetium(V). The molecular geometry and atom numbering of the $[\text{TcN}(\text{C}_9\text{H}_6\text{NS})_2]$ molecule are shown in Figure 1. Interatomic bond distances and angles, with esd's derived from the refinement, are given in Table II.

The coordination environment of technetium is distorted square pyramidal with the nitrido nitrogen atom at the apical position.

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Table II. Interatomic Bond Distances and Bond Angles in Bis(8-quinolinethiolato)nitridotechnetium(V)

Distances, Å			
Tc-N(1)	2.135 (2)	C(5)-C(6)	1.370 (5)
Tc-N(2)	1.623 (4)	C(6)-C(7)	1.403 (6)
Tc-S(1)	2.3559 (7)	C(7)-C(8)	1.382 (4)
N(1)-C(1)	1.336 (4)	C(8)-C(9)	1.423 (4)
N(1)-C(9)	1.382 (3)	C(1)-H(1)	0.99 (4)
S(1)-C(8)	1.762 (3)	C(2)-H(2)	1.13 (8)
C(1)-C(2)	1.400 (5)	C(3)-H(3)	0.96 (4)
C(2)-C(3)	1.363 (5)	C(5)-H(5)	0.87 (6)
C(3)-C(4)	1.422 (4)	C(6)-H(6)	1.02 (4)
C(4)-C(5)	1.421 (4)	C(7)-H(7)	0.84 (4)
C(4)-C(9)	1.421 (4)		
Angles, deg			
N(1)-Tc-N(2)	98.98 (6)	C(3)-C(4)-C(5)	123.3 (3)
N(1)-Tc-S(1)	82.16 (6)	C(3)-C(4)-C(9)	117.9 (3)
N(2)-Tc-S(1)	112.19 (2)	C(5)-C(4)-C(9)	118.9 (3)
N(1)-Tc-N(1')	162.0 (1)	C(4)-C(5)-C(6)	119.8 (3)
S(1)-Tc-S(1')	135.61 (5)	C(5)-C(6)-C(7)	121.3 (3)
C(1)-N(1)-Tc	121.4 (2)	C(6)-C(7)-C(8)	121.0 (3)
C(1)-N(1)-C(9)	118.5 (3)	C(7)-C(8)-C(9)	118.7 (3)
C(9)-N(1)-Tc	119.9 (2)	S(1)-C(8)-C(7)	122.2 (2)
C(8)-S(1)-Tc	100.2 (1)	S(1)-C(8)-C(9)	119.1 (2)
N(1)-C(1)-C(2)	123.2 (3)	C(4)-C(9)-N(1)	121.2 (2)
C(1)-C(2)-C(3)	119.4 (3)	C(8)-C(9)-N(1)	118.5 (3)
C(2)-C(3)-C(4)	119.7 (3)	C(4)-C(9)-C(8)	120.3 (2)

The 8-quinolinethiolato ligands are arranged with the like donor atoms diametrically opposed. These atoms are markedly distorted from coplanarity with $N(2)\equiv Tc-S(1)$ [$112.19(2)^\circ$] greater than $N(2)\equiv Tc-N(1)$ [$98.98(6)^\circ$]. The $N(1)-Tc-N(1')$ angle [$162.0(1)^\circ$] is thus greater than the $S(1)-Tc-S(1')$ angle [$135.61(5)^\circ$].

The $Tc^V\equiv N$ bond distance in $[TcN(C_9H_6NS)_2]$ is $1.623(4)$ Å. This is significantly longer than that of $1.604(6)$ Å in the square-pyramidal $[TcN(S_2CNET_2)_2]$ complex⁴ and similar to the $1.629(4)$ Å distance in the octahedral $[TcN(NCS)_2(CH_3CN)(PPh_3)_2]$ complex.⁶ In this latter case the nitrido nitrogen atom is trans to a weakly bonded acetonitrile molecule. These $Tc^V\equiv N$ distances are all longer than the $1.581(5)$ and $1.596(6)$ Å $Tc^{VI}\equiv N$ distances in $AsPh_4[TcNCl_4]$ and $AsPh_4[TcNBr_4]$, respectively.^{9,27}

The $Tc-S-C$ angles in $[TcN(C_9H_6NS)_2]$ are $100.2(1)^\circ$, which compare with the $Tc-S-C$ angles of close to 90° [average angle of $87.6(1)^\circ$] in $[TcN(S_2CNET_2)_2]$.⁴ The hybridization state of the S atoms in $[TcN(S_2CNET_2)_2]$ therefore contains less s-orbital character than it does in $[TcN(C_9H_6NS)_2]$, and this is in agreement with the $Tc-S$ distances that are greater, with an average value of $2.401(1)$ Å, in $[TcN(S_2CNET_2)_2]$ than $2.3559(7)$ Å in $[TcN(C_9H_6NS)_2]$.

Angles about the quinoline-N atom, N(1), in $[TcN(C_9H_6NS)_2]$ are close to 120° , ranging from $118.5(3)$ to $121.4(2)^\circ$, as expected for the sp^2 hybridization of this atom. By comparison, angles about the quinoline-N atom in the six-coordinate $[Tc^V(O)(CH_3C_9H_5NO)_2Cl]$ complex ($CH_3C_9H_5NO = 2$ -methyl-8-quinolinolate) vary considerably from 120° , ranging from $108.1(2)$ to $132.8(3)^\circ$.²³ Presumably, constraints arising from the presence of an oxygen rather than a sulfur donor atom impose less than ideal geometry for maximum overlap of the nitrogen σ -donor orbital with technetium. Indeed, the $Tc-N$ (quinoline) bond distance in $[TcN(C_9H_6NS)_2]$ of $2.135(2)$ Å is significantly less than those of $2.179(3)$ and $2.215(3)$ Å in $[TcO(CH_3C_9H_5NO)_2Cl]$.²³ The bite of the 8-quinolinethiolato ligand in $[TcN(C_9H_6NS)_2]$ is $82.16(6)^\circ$ whereas the oxygen analogue, 2-methyl-8-quinolinol, in $[TcO(CH_3C_9H_5NO)_2Cl]$ has bites of $80.7(1)$ and $76.2(1)^\circ$.

The N and S donor atoms of the 8-quinolinethiolato ligands are not coplanar. A plane calculated through any three of these atoms results in the fourth atom being ca. 1.08 Å out of the plane. This distortion from ideal square-pyramidal geometry can be described in terms of the "twist angle" of the two Tc,N,S planes (where N and S are part of the same bidentate ligand). This twist angle (defined as the sum of the angles by which the normals to the Tc,N,S planes deviate from the plane containing the nitrido N atom and the midpoints of the N and S atoms of each bidentate ligand) is 18.9° .

Each 8-quinolinethiolato ligand is planar to a high degree, and none of the 11 non-hydrogen atoms (including the sulfur atom) deviates by more than $0.022(3)$ Å from the mean plane.

Registry No. $Cs_2[TcNCl_5]$, 99376-44-0; $AsPh_4[TcNBr_4]$, 95012-28-5; $AsPh_4[TcNCl_4]$, 95012-25-2; $[NEt_4][TcN(NCS)_4(CH_3CN)]$, 99376-46-2; $[TcN(S_2CNET_2)_2]$, 77933-43-8; $[TcN(C_9H_6NS)_2]$, 99376-47-3; $[TcNCl_2(PPh_3)_2]$, 77933-40-5; $NH_4[TcO_4]$, 34035-97-7.

Supplementary Material Available: Listings of atomic temperature factors and observed and calculated structure factors for $[TcN(C_9H_6NS)_2]$ (18 pages). Ordering information is given on any current masthead page.

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