atoms, Mo1, are most affected by changes in the number of cluster electrons.

Reasons for the elongation of only two opposite bonds are not immediately apparent. Recently, molecular orbital calculations were made on similar *molecular* tetrameric Mo atom clusters containing 10-electron ($C_{2h}$—all five bonds of equal length) and 8-electron ($C_i$—two opposite bonds elongated) environments.[21] These show that such a unique distortion can arise from a second-order Jahn–Teller effect. Another explanation for the observed distortion could be the affects of Mo d–O p $\pi$ bonding, which would involve the sp$^2$-like interchain oxygen atoms. For these atoms in the clusters of $K_2Mo_8O_{16}$ and $Ba_{1.14}Mo_8O_{16}$, three criteria were examined: the length of the Mo–O bonds; the alignment of the oxygen lone pair with molybdenum atom d orbitals; and the sum of the bond strengths[22] around each oxygen atom. Even though the Mo1–O8 bond lengths are the shortest, O8 does not appear to have good positioning for $\pi$ bonding. Also, the valence sums of 1.85 ($K_2Mo_8O_{16}$) and 1.90 ($Ba_{1.14}Mo_8O_{16}$) for O8 imply an overall weaker bonding to molybdenum than expected (i.e., a valence sum of 2.0). The only interactions that optimize the three criteria are Mo1–O3 and Mo2–O3. These have relatively short bond lengths, good $\pi$ alignment, and bond strength sums greater than 2.1. Note that O3 is doubly bridging along an outside edge of the $Mo_4O_{16}$ cluster. The lone pair on O3 may effectively overlap with a "nonbonding" d orbital on Mo1 as well as with a d orbital on Mo2. The latter is an orbital that participates in the pair of Mo–Mo bonds in question. As the number of metal cluster electrons decreases, the Mo2–O3 $\pi$ interactions may increase, thereby raising the energy of the orbitals involved in the Mo1–Mo2 and Mo1′–Mo2′ bonds and stabilizing the observed distorted Mo atom configuration. Atom O4 appears to be well positioned for $\pi$ overlap with the d orbital on Mo1 that forms the elongated Mo–Mo bonds. However, the Mo1–O4 distances are not unusually short, and the valence sums for O4 are low with values of approximately 1.7.

Only a very simple description of the Mo–O bonding has been given here. Molecular orbital or band calculations would give insight into the role of molybdenum–oxygen $\pi$ bonding on the deformation process within these $Mo_4O_{16}$ clusters.

**Registry No.** $K_2Mo_8O_{16}$, 92014-66-9.

**Supplementary Material Available:** Listings of atomic thermal parameters and structure structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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# Chemistry and Structure of Hexakis(thiourea-*S*)technetium(III) Trichloride Tetrahydrate, $[Tc(SC(NH_2)_2)_6]Cl_3.4H_2O$

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The preparation and characterization of hexakis(thiourea-*S*)technetium(III) trichloride tetrahydrate, $[Tc(SC(NH_2)_2)_6]Cl_3.4H_2O$ (A), is described. Crystals of A are monoclinic, *C*2/*c*, with *a* = 11.876 (2) Å, *b* = 12.048 (2) Å, *c* = 19.662 (3) Å, and $\beta$ = 95.32 (1)°, and have four formula units in the unit cell. The structure was determined by standard methods and refined to $R_1 = 0.0391$, $R_2 = 0.0452$ on the basis of 1753 independent reflections. Data were measured with use of Mo K$\alpha$ radiation and a Syntex P2$_1$ diffractometer. The cation is roughly octahedrally coordinated by the six sulfur atoms of the thiourea groups. The Tc–S bonds (2.431 (1), 2.412 (1), 2.440 (1) Å) are significantly longer than Tc(V)–S lengths reported previously, but bond lengths within the thiourea groups are normal. The structure is held together by an extensive hydrogen-bonding network. Chemical reactions of A are described, as well as the preparation and characterization of $[Tc(SC(NH_2)_2)_6](BF_4)_3$, $[TcCl_2(diphos)_2]Cl\cdot 2H_2O$, $[Tc(CNC(CH_3)_3)_6]PF_6$, and $[Tc(P(OCH_3)_3)_6]PF_6$ from A.

## Introduction

The red-orange species formed by the reaction of the pertechnetate ion and thiourea in dilute mineral acids has been known since 1959.[2] The oxidation state of the technetium in this complex has been proposed by various workers to be Tc(VII), Tc(V), Tc(IV), or Tc(III).[3-5] No thorough study of the isolated complexes has, as yet, appeared. In this paper, we report the identification of these species as salts of the technetium(III) cation $[Tc^{III}(tu\text{-}S)_6]^{3+}$ (tu = thiourea). The crystal structure of $[Tc^{III}(tu\text{-}S)_6]Cl_3\cdot 4H_2O$ and the reactions of the cation with various ligands are described.

## Experimental Section

Technetium as $NH_4{}^{99}TcO_4$ was obtained as a gift from New England Nuclear (NEN), Billerica, MA. All manipulations were carried out in laboratories approved for low-level radioactivity ($^{99}$Tc is a weak $\beta$-emitter with a half-life of $2.12 \times 10^5$ years and particle energy of 0.292 MeV). All precautions followed have been detailed elsewhere.[6-8]

Infrared spectra were recorded in the range 4000–300 cm$^{-1}$ on a Perkin-Elmer PE180 grating infrared spectrophotometer as KBr pellets. Optical spectra, in solution, were measured with a Cary 17 spectrophotometer. Conductivity measurements were performed in methanol and acetonitrile by using a Yellow Springs Model 3403 conductivity cell and a Beckman RC-16C conductivity bridge. Magnetic susceptibility measurements were made on methanol solutions via the Evans NMR method[9] using a Varian T-60 spectrometer. The $^1$H NMR measurements were also made on the T-60 with $Me_4Si$ as the internal calibrant. $^{31}$P NMR measurements were made on a JEOL 90Q 90-MHz spectrometer with $H_3PO_4$ as an external reference. Melting points were obtained with a Mel-Temp apparatus

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and are uncorrected. The field desorption mass spectra were measured with a Varian MAT 731 instrument described elsewhere.[10] Before use, distilled water was passed through a Barnstead Ultrapure D8902 cartridge, followed by redistillation in a Corning AG-1 water still. The thiourea (MCB) was used as received; 1,2-bis(diphenylphosphino)ethane(diphos) was obtained from Strem Chemicals, Inc., Newburyport, MA, and *tert*-butyl isocyanide was prepared by a literature method.[11] Absolute ethanol was used throughout. All other chemicals were used without further purification unless otherwise specified. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA, and by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

**Preparation of the Complexes. Hexakis(thiourea-*S*)technetium(III) Trichloride.** To a 50-mL beaker containing a magnetic stirring bar were added ethanol (25 mL), 12 N HCl (4 mL), and thiourea (0.88 g, 11.6 mmol). To the stirred solution was added $NH_4TcO_4$ (1 mL, 0.469 M) after the thiourea had dissolved. The solution immediately turned dark brown. The color of the reaction mixture gradually turned red-orange during 2 h. At this time a red-orange solid had precipitated, which was isolated by suction filtration, washed with cold ethanol (2 × 5 mL), and dried in vacuo: yield of $[Tc(tu\text{-}S)_6]Cl_3$ 0.28 g (0.42 mmol), 90% based on Tc; mp 174 °C dec. This material is slightly soluble in ethanol and moderately soluble in methanol. The complex decomposes slowly in water. The material was recrystallized from 2 N HCl that contained thiourea (ca. 0.18 M) by chilling the solution for 4 days at −5 °C. The crystals, as deep red blocks, used for the X-ray structural analysis were collected on a filter and were not dried. The analytical sample was crushed and dried in vacuo.

Anal. Calcd for $C_6H_{24}Cl_3N_{12}S_6Tc$: C, 10.88; H, 3.66; Cl, 16.06; N, 25.39; S, 29.05. Found: C, 10.84; H, 3.59; Cl, 16.05; N, 25.30; S, 29.04. Optical spectrum in methanol: 493 nm ($\epsilon = 5.8 \times 10^3$ L mol$^{-1}$ cm$^{-1}$), 428 nm ($\epsilon = 7.4 \times 10^3$ *L* mol$^{-1}$ cm$^{-1}$), 233 nm ($\epsilon = 5.7 \times 10^4$ L mol$^{-1}$ cm$^{-1}$). IR spectrum (KBr): 3280 (s), 3190 (s), 1630 (s), 510 (w), 1100 (w), 685 (m), 570 (m), 465 (m) cm$^{-1}$. Conductivity (methanol, $10^{-3}$ M): $\Lambda_M = 260\ \Omega^{-1}$ cm$^2$ mol$^{-1}$. Magnetic moment: $\mu_{eff}(308\ K) = 2.7\ \mu_B$.

**Hexakis(thiourea-*S*)technetium(III) Tetrafluoroborate.** To a 50-mL beaker containing a magnetic stirring bar were added thiourea (1.31 g, 17.2 mmol) and 48–50% $HBF_4$ (20 mL). To the stirred solution was added 2.0 mL of 0.469 M $NH_4TcO_4$ (0.938 mmol) after the thiourea had dissolved. After 2 h of stirring, a bright red-orange crystalline solid had formed. This material was isolated by suction filtration, washed with cold $HBF_4$ (2 × 5 mL) and ether/ethanol (5 mL, 10:1 v/v), and dried in vacuo: yield of $[Tc(tu\text{-}S)_6](BF_4)_3$ 0.63 g (0.77 mmol), 82% based on Tc; mp 178–180 °C dec. This compound is soluble in methanol, ethanol, acetonitrile, and acetone.

Anal. Calcd for $C_6H_{24}B_3F_{12}N_{12}S_6Tc$: C, 8.83; H, 3.97; N, 20.60; S, 23.57. Found: C, 8.63; H, 3.19; N, 20.19; S, 23.19. Optical spectrum in methanol: 493 nm ($\epsilon = 6.8 \times 10^3$ L mol$^{-1}$ cm$^{-1}$), 428 nm ($\epsilon = 8.2 \times 10^3$ L mol$^{-1}$ cm$^{-1}$), 233 nm ($\epsilon = 6.2 \times 10^4$ L mol$^{-1}$ cm$^{-1}$). IR spectrum (KBr): similar to that of $[Tc(tu\text{-}S)_6]Cl_3$ except for a broad band at 1070 cm$^{-1}$ caused by the $BF_4^-$ ion. Conductivity (acetonitrile, $10^{-3}$ M): $\Lambda_M = 347\ \Omega^{-1}$ cm$^2$ mol$^{-1}$. Magnetic moment: $\mu_{eff}(308\ K) = 2.7\ \mu_B$.

**Dichlorobis(1,2-bis(diphenylphosphino)ethane)technetium(III) Chloride Dihydrate.** To a 50-mL round-bottom flask containing a magnetic stirring bar were added $[Tc(tu\text{-}S)_6]Cl_3$ (0.16 g, 0.24 mmol), methanol (35 mL), and 12 N HCl (0.5 mL). When all the starting material had dissolved, diphos (0.45 g, 1.13 mmol) was added to the stirred solution. The reaction mixture was then heated to reflux. After 1 h, the optical spectrum of an aliquot of the reaction mixture had an intense absorption band at 475 nm, characteristic of the $[Tc(diphos)_2Cl_2]^+$ ion.[12] The reaction mixture was then cooled to room temperature, and solvent was removed in vacuo until its volume was 20 mL. At this point the solution was filtered and 12 N HCl (4 mL) was added to the orange filtrate. After the filtrate was allowed to stand at 5 °C for 48 h, red-orange needles formed, which were isolated by suction filtration, washed with ether/ethanol (5 mL 10:1 v/v), and dried in vacuo. The yield of $[Tc(diphos)_2Cl_2]Cl{\cdot}2H_2O$ was 0.08 g (0.08 mmol), 33% based on Tc. Anal. Calcd for $C_{52}H_{52}Cl_3O_2P_4Tc$: C, 60.12; H, 5.06; Cl, 10.24. Found: C, 60.38; H, 5.12; Cl, 10.47.

**Hexakis(*tert*-butyl isocyanide)technetium(I) Hexafluorophosphate.** To a 50-mL round-bottom flask containing a stir bar were added $[Tc(tu\text{-}S)_6]Cl_3$ (0.84 g, 0.13 mmol), methanol (25 mL), and *tert*-butyl isocyanide (1.1 g, 1.3 mmol). The stirred reaction mixture was refluxed for 1.5 h. The pale yellow solution was then transferred to a 100-mL beaker, and water (40 mL) was added. The solution was concentrated to half its volume. At this point water (30 mL) was added to the hot solution, and its volume was again halved. The almost colorless solution was cooled to room temperature, and $NH_4PF_6$ (0.5 g) in water (10 mL) was added, precipitating a white solid. The solid was collected by suction filtration, washed with water (10 mL) and ether (10 mL), and dried in vacuo: yield of $[Tc(t\text{-}BuNC)_6]PF_6$ 0.06 g, 0.08 mmol, 62% based on Tc; mp 222 °C dec. The complex is soluble in polar organic solvents and was recrystallized by slow evaporation of an acetone/water (4:1 v/v) solution, yielding white crystals. Anal. Calcd for $C_{30}H_{54}F_6N_6PTc$: C, 48.50; H, 7.34; N, 11.32. Found: C, 48.60; H, 7.25; N, 11.32. Optical spectrum in acetonitrile: 260 (sh), 235 nm ($\epsilon = 8.0 \times 10^4$ L mol$^{-1}$ cm$^{-1}$). IR (KBr): $\nu_{CN}$ 2080 (s), 2045 (sh) cm$^{-1}$. Conductivity (acetonitrile, $10^{-3}$ M): $\Lambda_M = 140\ \Omega^{-1}$ cm$^2$ mol$^{-1}$. FDMS (positive ion mode): *m/z* 597.

**Reaction of $[Tc(tu\text{-}S)_6]Cl_3$ with $NH_4SCN$.** To a 50-mL round-bottom flask were added 0.03 g of $[Tc(tu\text{-}S)_6]Cl_3$ (0.05 mmol), a stir bar, and methanol (20 mL). To the deep orange solution was added $NH_4SCN$ (0.80 g, 10.5 mmol). The stirred solution was refluxed for 30 min. The optical spectrum of the resulting orange-yellow reaction mixture had a strong absorption at 412 nm, characteristic of the $[Tc(NCS)_6]^{3-}$ ion.[13]

**Hexakis(trimethyl phosphite)technetium(I) Hexafluorophosphate.** To a 100-mL round-bottom flask containing a magnetic stirring bar were added $[Tc(tu\text{-}S)_6]Cl_3$ (0.17 g, 0.26 mmol), methanol (40 mL), and trimethyl phosphite (3 mL, 22 mmol). The stirred solution was heated to reflux. After 2.5 h, the pale violet solution was allowed to cool to room temperature. The solvent was removed under vacuum. The residue was dissolved in 60 mL of acetone/water (1:1 v/v), and $NH_4PF_6$ (0.5 g) dissolved in water (5 mL) was added. This solution slowly evaporated, yielding off-white crystals, which were recrystallized by evaporation of an acetone/water (1:1 v/v) solution. The resulting white crystals were separated by filtration, washed with water (5 mL), and dried in vacuo: yield of hexakis(trimethyl phosphite)technetium(I) hexafluorophosphate 0.08 g (0.08 mmol), 31% based on Tc; mp, > 115 °C dec. This compound is soluble in polar organic solvents. Anal. Calcd for $C_{18}H_{54}F_6O_{18}P_7Tc$: C, 21.87; H, 5.52; P, 21.93. Found: C, 22.03; H, 5.35; P, 21.78. Optical spectrum in acetonitrile: 212 nm ($\epsilon = 12.2 \times 10^4$ L mol$^{-1}$ cm$^{-1}$). IR (KBr): 2945 (m), 2840 (m), 1460 (m), 1170 (m), 1050 (vs), 845 (s), 770 (s), 690 (s), 535 (s) cm$^{-1}$. Conductivity (acetonitrile, $10^{-3}$ M): $\Lambda_M = 136\ \Omega^{-1}$ cm$^2$ mol$^{-1}$. $^1$H NMR ($CHCl_3\text{-}d_1$); 3.63 ppm (sharp multiplet). $^{31}P\{^1H\}$ NMR ($CHCl_3\text{-}d_1$): 266.8–41.8 ppm (decet) for the $[Tc(PO(CH_3)_3)_6]^+$ cation, $J_{P\text{-}Tc} = 910$ Hz; −86.4 to −203.5 ppm (septet), $J_{P\text{-}F} = 708$ Hz. FDMS (positive ion mode): *m/z* 843, 719.

**Collection of the Crystal Data.** Precision photographs showed the red crystal was monoclinic. Unit cell parameters were obtained from a least-squares fit of $\chi$, $\phi$, and 2 $\theta$ for 15 reflections in the range 18.3° < $2\theta$ < 26.4° recorded on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ 0.71069 Å). Crystal data and other numbers related to data collection are given in Table I. The density was obtained by flotation in a carbon tetrachloride/dibromomethane mixture. Intensities were also recorded on the Syntex $P2_1$ diffractometer with a coupled $\theta$(crystal)–$2\theta$(counter) scan. The methods of selection of scan rates and initial data treatment have been described.[14,15] Corrections were made for Lorentz–polarization effects but not for absorption. This will make a maximum error of <3.0% in $F_o$.

**Solution of the Structure.** The coordinates of the technetium atom were found from a three-dimensional Patterson synthesis, and since Tc appeared to lie on an inversion center, the alternate space group *Cc* was rejected. The space group choice was justified by the successful solution of the structure. A series of full-matrix least-squares re-

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**Table I.** Crystal Data

| | |
|---|---|
| compd | $[Tc(SC(NH_2)_2)_6]Cl_3 \cdot 4H_2O$,<br>$C_6H_{32}Cl_3N_{12}O_4S_6Tc$ |
| fw | 734.02 |
| cryst shape and size, mm | needle, $r = 0.075$, $l = 0.30$ |
| systematic absences | $hkl$, $h + k = 2n + 1$;<br>$h0l$, $l = 2n + 1$ |
| space group | $C2/c$ |
| unit cell | |
| $a$, Å | 11.876 (2) |
| $b$, Å | 12.048 (2) |
| $c$, Å | 19.662 (3) |
| $\beta$, deg | 95.32 (1) |
| $V$, Å$^3$ | 2801.3 |
| $Z$ | 4 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.74 |
| $\rho_{obsd}$, g cm$^{-3}$ | 1.74 (1) |
| linear abs coeff, cm$^{-1}$ | 12.55 |
| max $2\theta$, deg | 45 |
| reflcns measd | $\bar{h}, \bar{k}, \pm l$ |
| std reflcns (esd) | $\bar{2}62$ (0.022), $\bar{3}\bar{5}1$ (0.018) |
| temp, °C | 22 |
| no. of independent reflcns | 1836 |
| no. of reflcns with $I > 0$, used in refinements | 1753 |
| no. of variables | 95 |
| final $R_1, R_2$$^a$ | 0.0391, 0.0452 |
| final shift/error max (av) | 0.002 (0.00036) |
| $x$ (secondary extinction) | 0.00072 |
| final diff map max, min, e Å$^{-3}$ | 0.73, −0.50 |
| weighting | $w = (\sigma(F)^2 + 0.000416F_o^2)^{-1}$ |
| error in an obsn of unit wt | 0.9126 |

$^a$ $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

**Table II.** Atomic Positional Parameters ($\times 10^4$)

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Tc | 2500 | 2500 | 5000 |
| Cl(1) | 2155 (1) | 5611 (1) | 3330 (1) |
| Cl(2) | 5000 | 4584 (2) | 2500 |
| S(1) | 3862 (1) | 3213 (1) | 4260 (1) |
| S(2) | 2373 (1) | 4450 (1) | 5260 (1) |
| S(3) | 3934 (1) | 1987 (1) | 5916 (1) |
| C(1) | 4910 (4) | 2299 (4) | 4059 (2) |
| C(2) | 2344 (4) | 4787 (4) | 6121 (2) |
| C(3) | 4939 (4) | 2974 (4) | 6183 (2) |
| N(11) | 5189 (4) | 1392 (3) | 4413 (2) |
| N(12) | 5455 (4) | 2550 (4) | 3527 (2) |
| N(21) | 2381 (3) | 4057 (4) | 6613 (2) |
| N(22) | 2277 (4) | 5860 (4) | 6252 (2) |
| N(31) | 5598 (4) | 2748 (4) | 6735 (2) |
| N(32) | 5065 (4) | 3926 (4) | 5857 (2) |
| O(1) | 2653 (3) | 3282 (3) | 2612 (2) |
| O(2) | 0 | 4312 (4) | 2500 |
| O(3)$^a$ | 2274 (9) | 2248 (9) | 179 (5) |

$^a$ This atom was disordered and was given half-occupancy in the given position.

finements followed by three-dimensional electron difference syntheses revealed all the non-hydrogen atoms. Temperature factors for Tc, S, and Cl were made anisotropic, and further refinement of all parameters for non-hydrogen atoms with full-matrix least-squares methods, minimizing $\sum w(|F_o| - |F_c|)^2$, was terminated when the maximum shift/error was <0.2. At this stage the positional parameters of the hydrogen atoms were included for two cycles to give a rough estimate of the errors. Further refinement, not varying the hydrogen atoms, was terminated with a maximum shift/error of 0.002. Corrections were made for secondary extinction by using the SHELX method. Throughout, the scattering curves were taken from ref 16, and anomalous dispersion corrections from ref 17 were applied to the curves for Tc, S, and Cl. The atom parameters for non-hydrogen atoms are listed in Table II.[18]

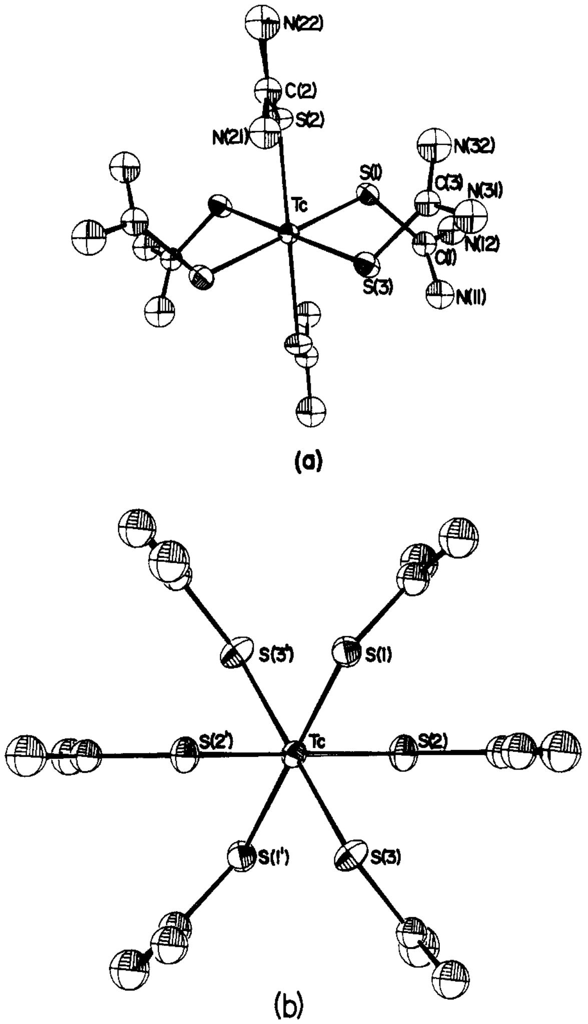

**Figure 1.** (a) The cation hexakis(thiourea-*S*)technetium(III) showing the atom numbering. The technetium atom is at an inversion center. (b) The view down the pseudo-$\bar{6}$ axis.

## Results and Discussion

There are numerous examples of thiourea being oxidized by metal complexes.[19,20] One well-documented case of this is the reaction of $OsO_4$ with thiourea in dilute mineral acids to form the $[Os(tu)_6]^{3+}$ ion and formamidine disulfide.[21] The reaction of $KReO_4$ with thiourea in concentrated HCl produced the Re(V) complex $(ReO(H_2O)Cl_2(tu)_2)Cl$.[22] The only Re(III) complexes of thiourea known are the neutral species $Re(tu)_3X_3$ (X = Cl, Br) made from the reaction of $[Re_2X_8]^{2-}$ with thiourea in methanolic HX.[23] The rhenium analogue of the technetium complex described here is not known. This technetium complex, formed in the spectrophotometric assay of technetium using thiourea and dilute mineral acids, has been isolated in high yield and has been shown to be the hexakis(thiourea-*S*)technetium(III) cation. It has been isolated and

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(18) All computations were carried out on a CYBER 170-730 computer. Programs used for initial data treatment were from the XRAY 76 package (Stewart, J. M. Technical Report TR-446; University of Maryland: College Park, MD, 1976). The structure was solved with SHELX (Sheldrick, G. M. "SHELX"; Cambridge University: Cambridge, England, 1976). Planes were calculated by using NRC-22 (Ahmed, F. R.; Pippy, M. E. "NRC-22"; National Research Council of Canada: Ottawa, Canada, 1981). Diagrams were prepared ORTEPII (Johnson, C. K. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976).

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**Table III.** Selected Interatomic Distances (Å) and Angles (deg)

| | | | | | |
|---|---|---|---|---|---|
| | | Non-Hydrogen Bond Distances | | | |
| Tc-S(1) | 2.431 (1) | Tc-S(2) | 2.412 (1) | Tc-S(3) | 2.440 (1) |
| S(1)-C(1) | 1.735 (5) | S(2)-C(2) | 1.744 (5) | S(3)-C(3) | 1.732 (5) |
| C(1)-N(11) | 1.320 (6) | C(2)-N(21) | 1.305 (6) | C(3)-N(31) | 1.307 (6) |
| C(1)-N(12) | 1.316 (7) | C(2)-N(22) | 1.323 (6) | C(3)-N(32) | 1.329 (7) |
| | | Hydrogen Bond Distances | | | |
| N(11)···Cl(1) | 3.433 (5) | N(11)-H(11) | 0.89 (8) | H(11)···Cl(1) | 2.65 (8) |
| N(12)···Cl(1) | 3.135 (5) | N(12)-H(13) | 1.01 (8) | H(13)···Cl(1) | 2.18 (8) |
| N(12)···Cl(2) | 3.189 (5) | N(12)-H(14) | 0.93 (8) | H(14)···Cl(2) | 2.27 (8) |
| N(21)···Cl(1) | 3.435 (4) | N(21)-H(21) | 1.06 (7) | H(21)···Cl(1) | 2.39 (7) |
| N(22)···O(1) | 2.863 (6) | N(22)-H(23) | 0.78 (8) | H(23)···O(1) | 2.24 (8) |
| N(22)···O(3) | 3.106 (12) | N(22)-H(24) | 0.89 (8) | H(23)···O(3) | 2.27 (8) |
| N(31)···O(2) | 3.020 (6) | N(31)-H(31) | 0.78 (8) | H(31)···O(2) | 2.25 (8) |
| N(31)···Cl(1) | 3.334 (5) | N(31)-H(32) | 0.89 (8) | H(32)···Cl(1) | 2.47 (8) |
| O(1)···Cl(2) | 3.224 (4) | O(1)-H(1) | 0.82 (8) | H(1)···Cl(2) | 2.43 (8) |
| O(1)···Cl(1) | 3.221 (4) | O(1)-H(2) | 0.72 (8) | H(2)···Cl(1) | 2.75 (8) |
| O(2)···Cl(1) | 3.300 (3) | O(2)-H(4) | 1.0 (1) | H(4)···Cl(1) | 2.5 (1) |
| | | Angles | | | |
| S(1)-Tc-S(2) | 99.18 (4) | S(1)-Tc-S(3) | 85.78 (4) | S(2)-Tc-S(3) | 98.22 (4) |
| Tc-S(1)-C(1) | 116.3 (2) | Tc-S(2)-C(2) | 116.1 (2) | Tc-S(3)-C(3) | 117.7 (2) |
| S(1)-C(1)-N(11) | 123.8 (4) | S(2)-C(2)-N(21) | 124.1 (4) | S(3)-C(3)-N(31) | 116.8 (4) |
| S(1)-C(1)-N(12) | 116.8 (4) | S(2)-C(2)-N(22) | 115.1 (4) | S(3)-C(3)-N(32) | 123.5 (4) |
| N(11)-C(1)-N(12) | 119.4 (5) | N(21)-C(2)-N(22) | 120.8 (4) | N(31)-C(3)-N(32) | 119.7 (4) |

characterized as both its chloride and tetrafluoroborate salts. An X-ray crystallographic study of the isolated complex $[Tc(tu\text{-}S)_6]Cl_3·4H_2O$ has shown that the six thiourea molecules are S bonded to the technetium atom (see below).

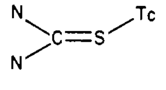
In both the chloride and tetrafluoroborate salts of the complex, the band in the infrared spectrum at 683 $cm^{-1}$ is assigned to a C═S stretching and N—C—N bending mode that occurs at 730 $cm^{-1}$ in free thiourea. The shift of this band to lower energy upon complex formation has been interpreted as a sign of S bonding in thiourea coordination complexes.[24] There is no evidence for a Tc═O, $Tc_2O_3$, or $TcO_2$ linkage in the infrared spectrum. Conductivity measurements in both methanol and acetonitrile are consistent with the formulation of the complex as a 3:1 electrolyte.[25] The observed magnetic moment for both the chloride and tetrafluoroborate salts of the complex, 2.7 $\mu_B$ at 308 K, is in the range expected for a $d^4$ ion with two unpaired electrons.[26]

The molecular cation is illustrated in Figure 1, and interatomic distances and angles are given in Table III. Although the technetium atom sits on an inversion center and is, superficially, octahedrally coordinated to six sulfur atoms, there are some significant distortions. Thus, the S–Tc–S angles all differ significantly from 90° (range 4.2–9.2°). All Tc–S distances are, as expected, greater than values measured for Tc(V)–S bonds (range 2.283 (4) –2.336 (4) Å),[8,27,28] but there are large internal differences. While Tc–S(1) (2.431 (2) Å) is only 6.4$\sigma$ ($\sigma = (\sigma_2^2 + \sigma_2^2)^{1/2}$) shorter than Tc–S(3) (2.440 (1) Å), Tc–S(2) (2.412 (1) Å) is shorter than Tc–S(1) by 13.4$\sigma$ and Tc–S(3) by 19.8$\sigma$.

We can consider various reasons for the observed distortion distortion such as sulfur–sulfur interactions, Jahn–Teller distortion, or packing requirements. We can eliminate sulfur–sulfur interactions as a cause. If there were sulfur–sulfur interactions, these would be at the expense of Tc–S interactions, causing longer Tc–S distances. Any obseved effect is the wrong way around, however, since S(1) and S(3) have only one short S–S interaction, both to S(2) (3.140 (2) and 3.177 (2) Å), which thus has two such interactions. Similarly, an examination for hydrogen bonding to sulfur found no significant interactions. The most probable C(2)–S(2) distance is longer than C(1)–S(1) and C(3)–S(3), but the differences are well within the errors and are not significant.

For first-row transition metals a $d^4$ system in a relatively weak field should have a $^5E_g$ octahedral state, which will show a marked Jahn–Teller distortion. For the second-row elements, however, a spin-paired $^3T_{1g}$ ground state is expected and shown by the 2.7 $\mu_B$ magnetic moment, and here distortion should be less. Jahn–Teller distortion could remove the degeneracy in two ways, by a tetragonal distortion or a trigonal distortion. Both effects are present here. The short Tc(2)–S(2) bond clearly shows the tetragonal distortion. As shown in Figure 1b, however, the molecule has roughly $D_{3d}$ symmetry and the trigonal distortion is illustrated by contrasting the S···S nonbonding distances in the triangular faces perpendicular to the pseudo-$\bar{6}$ axis with those between the top and bottom faces[29] (S(2)···S(1′) 3.140 (3) Å, S(2)···S(3′) and S(1)···S(3) 3.315 (3) Å vs. S(1)···S(3′) 3.569 (3) Å, S(2)–S(3) 3.669 (3) Å, S(2)···S(1) 3.687 (3) Å) and also the related S–Tc–S angles (S(1)–Tc–S(2) 80.82 (4)°, S(2)–Tc–S(3) 81.78 (4)°, S(1)–Tc–S(3′) 85.78 (4)° vs. S(1′)–Tc–S(2) 99.18 (4)°, S(3)–Tc–S(2) 98.22 (4)°, S(1)–Tc–S(3) 94.22 (4)°). As can be seen in the diagram, even the orientation of the thiourea ligands reflects the $D_{3d}$ symmetry, all being oriented away from the $C_3$ axis in order to minimize repulsion. Ligand–ligand repulsions are an alternate explanation to the Jahn–Teller effect for this trigonal distortion.

The arrangement of the thiourea ligands is caused by steric requirements and the preference of the



system to be as nearly planar as possible. Only for the S(2) system is this achieved; the NNC/CSTc dihedral angle is 0.3 (5)°. For S(1) and S(3) there are significant distortions, and the corresponding dihedral angles are 18.3 (4) and 9.6 (4)°, respectively. There is then a strong steric interaction between one of the hydrogen atoms on the nitrogen atom cis to the technetium atom and the sulfur atoms. The thiourea planes are oriented to allow these hydrogen atoms to lie between the

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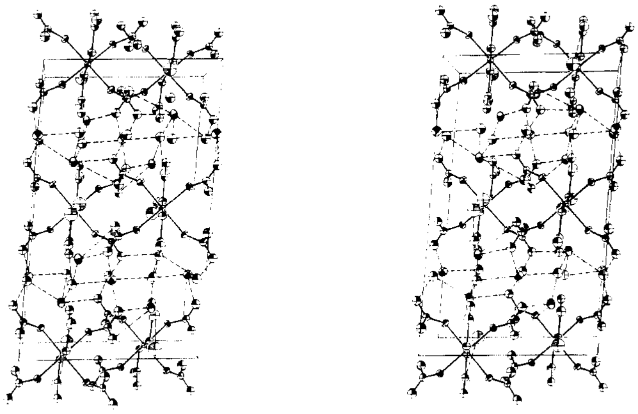

**Figure 2.** Packing of hexakis(thiourea-*S*)technetium(III) trichloride tetrahydrate within the unit cell. *a* and *c** are parallel to the bottom and sides of the page, respectively, and the view is down *b*. The hydrogen-bonding network is shown by dotted lines.

adjacent sulfur atoms. Thus H(33), H(22), and H(12) lie between the S(1), S(2), the S(1), S(3), and the S(2), S(3) pairs, respectively, causing the smallest STcSC torsional angles of very roughly 45° (actual range 25.7 (2)–56.6 (2)°). There is still a repulsive interaction, and this causes the NCS angles cis to Tc to be 7–9° greater than the corresponding trans angles.

The thiourea ligands are essentially planar. The average of the C–S distances is about 0.15 Å longer than values for thiourea,[30,31] and the C–N distances are about 0.02 Å shorter than in thiourea, but because of the errors in the various determinations these differences may not be significant. We assume that further deviations from idealized symmetry are caused by hydrogen bonding. There is a very extensive hydrogen-bonding network holding the crystal together, as shown in Figure 2. The cations lie in layers at $z = 0, {}^1/_2$, and the hydrogen-bonding network is centered at roughly $z = {}^1/_4, {}^3/_4$ and involves the two chloride ions, the O(1) and O(2) water molecules, and all of the amine groups except N(31). The third water molecule, O(3), is only involved in very weak hydrogen bonding and sits in holes in the cation layer. This accounts for the very high temperature factor and the disorder.

The $[Tc(tu\text{-}S)_6]^{3+}$ ion has been used to prepare several other low-valent technetium species. Aside from the known complexes $[Tc(diphos)_2Cl_2]^{+}$[12] and $[Tc(NCS)_6]^{3-}$,[13] the new compounds $[Tc(t\text{-}BuNC)_6]PF_6$ and $[Tc(P(OCH_3)_3)_6]PF_6$ were prepared in 62% and 31% yields, respectively. The isocyanide complex, like analogous, hexakis(alkyl isocyanide) complexes of univalent Mn and Re, is a white, air-stable crystalline solid.[32,33] The cation has been identified as the *m*/*z* 597 peak in the positive ion field desorption mass spectrum.[34] The reactions of $[Tc(tu\text{-}S)_6]^{3+}$ with diphos and $SCN^-$ to form Tc(III) species and with *tert*-butyl isocyanide and trimethyl phosphite to form stable Tc(I) complexes indicate that the thiourea molecules are easily replaced under relatively mild conditions. Because of its ease of preparation, its high yield, and the lability of the thiourea ligands, the title complex is likely to be a useful synthetic precursor in the lower valent chemistry of technetium.[35]

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**Registry No.** $[Tc(tu\text{-}S)_6]Cl_3$, 91467-29-7; $[Tc(tu\text{-}S)_6](BF_4)_3$, 91467-31-1; $[TcCl_2(diphos)_2]Cl$, 91467-32-2; $[Tc(t\text{-}BuNC)_6]PF_6$, 89172-45-2; $[Tc(P(OCH_3)_3)_6]PF_6$, 91467-34-4; $NH_4TcO_4$, 34035-97-7.

**Supplementary Material Available:** Listings of temperature factors, positional coordinates for hydrogen atoms, bond lengths and angles involving hydrogen, best planes and dihedral angles, and structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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