Contribution from the Department of Chemistry,
Boston College, Chestnut Hill, Massachusetts 02167

Sulfur Atom Transfer with Reduction of a $[Tc^{VI}{\equiv}N]^{3+}$ Core to a $[Tc^{I}{-}N{\equiv}S]^{2+}$ Core. Crystal Structure of *mer*-$[Cl_2(SN)(4\text{-pic})_3Tc]$

Jun Lu and M. J. Clarke*

Received March 14, 1990

The combination of pyridine ligands, $[NCl_4Tc]^-$ and dithionite results in transfer of an S atom to the coordinated nitride and a net five-electron reduction of the Tc to yield *mer*-$[(SN)Cl_2(py)_3Tc]$. The compound *mer*-$[(SN)Cl_2(pic)_3Tc]{\cdot}CHCl_3$ crystallizes in the orthorhombic space group $Pna2_1$, with cell parameters $a = 19.628$ (1) Å, $b = 11.848$ (3) Å, $c = 11.332$ (4) Å, $Z = 4$, and $R = 0.037$. The Tc—N≡S bond angle is 176 (1)°. The Tc—NS and the N≡S bond lengths are 1.73 (1) and 1.54 (1) Å, respectively.

While the transfer of oxygen atoms between transition metals and various substrates can be used to vary the metal oxidation state by ±2 and is important in catalytic processes,[1] reactions of the nitride in isoelectronic nitrido complexes usually results in a derivatized nitrogen. In only a few cases has the intermediate involving the association of the O atom receiving group been trapped, as occurs in the formation of some phosphine oxide complexes.[2] On the other hand, unusual thionitrosyl complexes of transition metals have been prepared by the transfer of S atoms from S_8 or S_2Cl_2 to nitrido ligands, resulting in a four-electron reduction of the metal center.[3,4] Thionitrosyl complexes of Tc^I, Tc^{II}, and Tc^{III} have been recently synthesized from a $[Tc^V{=}N]^{2+}$ core and S_2Cl_2.[5-8] In this work, we relate the formation of a new thionitrosyl complex of Tc^I prepared from a $[Tc^{VI}{\equiv}N]^{3+}$ core with dithionite as the S atom source and show from electrochemical correlations that $N{\equiv}S^+$ is nearly as effective at delocalizing electron density from Tc^I as $N{\equiv}O^+$.

Experimental Section

Caution! ^{99}Tc is a weak β emitter ($\beta = 0.292$ MeV) with $t_{1/2} = 2.12 \times 10^5$ years. All manipulations were carried out in laboratories approved for low-level radioactivity. Pyridine (py), 4-methylpyridine (pic), and 3,5-dimethylpyridine (lut) were obtained from Aldrich Chemical and used without further purification. The compound *mer*-$[(SN)Cl_2(pic)_3Tc]{\cdot}CHCl_3$, was synthesized by mixing 60 mg of $[Bu_4N][TcNCl_4]$[9] with 300 mg of $Na_2S_2O_4$ in 15 mL of 4-picoline. The mixture was heated to boiling for ~2 h, which reduced the volume to 2–3 mL. After cooling, 30 mL of $CHCl_3$ and 30 mL of H_2O were added to the mixture, which was shaken, and the $CHCl_3$ layer separated. After three $CHCl_3$ extractions were combined in this fashion, the total was dried by rotary evaporation. The residue was redissolved in a minimum of $CHCl_3$ and loaded onto a silica gel 60 chromatography column. The desired product was eluted with chloroform as a major green band, which was rotary evaporated to dryness and redissolved in chloroform. Single crystals of the compound resulted from slow diffusion of hexanes into a chloroform solution. Yield: 70%. Analyses were obtained on a sample stored in a vacuum desiccator, which removed the chloroform of solvation. Anal. Calcd for $H_{21}C_{18}N_4Cl_2STc$: H, 4.27; C, 43.65; N, 11.31; Cl, 14.32; Tc, 20.0. Found: H, 4.47; C, 43.81; N, 11.08; Cl, 14.15; Tc, 20.3. UV-visible peaks in $CHCl_3$ [λ, nm (ε, $M^{-1}\ cm^{-1}$)]: 375 (4300), 655 (100). IR (cm^{-1}): 1620 (s), 1503 (s), 1444 (s), 1426 (s), 1173 (vs, $\nu_{N{\equiv}S}$), 1032 (s), 815 (vs), 512 (s). FAB-MS (major peaks, *m/z*): 494 (parent, P), 459 (P − Cl), 401 (P − pic), 366 (P − Cl − pic), 334 (P − S − Cl − pic), 308 (P − 2pic), 273 (P − Cl − 2pic). $\mu_{eff} = 0.5\ \mu_B$. ^1H NMR ($CDCl_3$; δ, ppm): 2.43 [$CH_3(x)$], 7.17 [$H_\beta(x)$], 2.46 [$CH_3(y)$], 7.12 [$H_\beta(y)$], 8.55 [$H_\alpha(x)$], 8.18 [$H_\alpha(y)$]. For the NMR assignments, the Tc—N≡S axis was assigned as *z*, the Cl—Tc—pic axis as *y*, and the pic—Tc—pic axis as *x*.

Table I. Crystallographic Data for *mer*-$[(SN)Cl_2(pic)_3Tc]{\cdot}CHCl_3$

formula	$H_{22}C_{19}N_4SCl_5Tc$
fw	614.63
cryst dimens, mm	0.15 × 0.15 × 0.20
color	dark green
radiation source	Cu Kα, λ = 1.541 78 Å; graphite monochromated
μ, cm^{-1}; rel transm factors	101.2 (5); 0.86–1.0
space group	orthorhombic, $Pna2_1$ (No. 33)
cell consts, Å	$a = 19.628$ (1), $b = 11.848$ (3), $c = 11.332$ (4)
cell vol, $Å^3$	2635.4 (4)
Z (fw/unit cell)	4
d_{obs}, d_{calcd}, g/cm^3	1.556, 1.549
tot. no. of unique observns	2224
no. of obsd reflcns[a]	1421
scan mode	$\omega{-}2\theta$
$2\theta_{max}$, deg	118.7°
scan rate, deg/min in ω	32
scan width	1.42 + 0.30 tan (θ)
no. of variables in least-squares refin	270
$R = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$	0.037
$R_w{}^b = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum\lvert w(F_o)^2\rvert]^{1/2}$	0.046
goodness of fit = $[\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(N_{obsevn} - N_{param})]^{1/2}$	1.12

[a] T = 20 (1) °C. Reflections with $F_o > 3\sigma(F_o)$ were retained as observed and used in the solution and refinement of the structure. Three standard reflections were monitored with a limit of 0.2% variation. Function minimized was $\sum w(|F_o| - |F_c|)^2$. [b] Weighting scheme: $w = 4(F_o)^2[\sigma^2/F_o{}^2]^2$.

mer-$[(SN)Cl_2(py)_3Tc]$ was similarly prepared. Yield: 75%. Anal. Calcd for $H_{15}C_{15}N_4Cl_2STc$: H, 3.34; C, 39.76; N, 12.36; Cl, 15.65; Tc, 21.8. Found: H, 3.57; C, 40.01; N, 12.45; Cl, 15.39; Tc, 22.5. UV-visible peaks in $CHCl_3$ [λ, nm (ε, $M^{-1}\ cm^{-1}$)]: 370 (3900), 658 (100). IR (cm^{-1}): 1602 (s), 1482 (s), 1447 (vs), 1173 (vs, $\nu_{N{\equiv}S}$), 765 (s), 758 (vs), 695 (s). $\mu_B = 0.77\ \mu_B$. ^1H NMR ($CDCl_3$; δ, ppm): 7.79 [$H_\gamma(x)$], 7.75 [$H_\gamma(y)$], 7.39 [$H_\beta(x)$], 7.35 [$H_\beta(y)$], 8.72 [$H_\alpha(x)$], 8.36 [$H_\alpha(y)$].

mer-$[(SN)Cl_2(lut)_3Tc]$ was similarly prepared. Anal. Calcd for $H_{27}C_{21}N_4Cl_2STc$: H, 5.06; C, 46.94; N, 10.43; Cl, 13.20; Tc, 18.4. Found: H, 5.24; C, 47.41; N, 10.39; Cl, 13.44; Tc, 16.7. UV–visible peaks in $CHCl_3$ [λ, nm (ε, $M^{-1}\ cm^{-1}$)]: 376 (4400), 662 (140). IR (cm^{-1}): 1597 (s), 1461 (s), 1440 (s), 1173 (vs, $\nu_{N{\equiv}S}$), 1152 (s), 864 (s), 702 (s). $\mu_{eff} = 0.72\ \mu_B$. ^1H NMR ($CDCl_3$; δ, ppm): 2.28 [$CH_3(x)$], 2.23 [$CH_3(y)$], 8.35 [$H_\gamma(x)$], 7.33 [$H_\gamma(y)$], 8.35 [$H_\alpha(x)$], 7.33 [$H_\alpha(y)$].

Compound Characterization. All elemental analyses (except for ^{99}Tc) were performed by Galbraith Laboratories, Knoxville, TN. Technetium analyses were performed by radioscintillation counting.[10] Magnetic susceptibility studies were performed on a Cahn Model 7500 electrobalance equipped with a 14 502-G permanent magnet at 25 °C and corrected for the diamagnetic contributions of the atoms. UV–visible spectra were obtained on a Cary Model 2400 instrument. IR spectra were

---

(1) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401–1449.
(2) Abrams, M. J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1984**, *82*, 125–128.
(3) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; pp 342, 862.
(4) Bishop, M. W.; Chatt, J.; Dilworth, J. *J. Chem. Soc., Dalton Trans.* **1979**, 1–5.
(5) Kaden, L.; Lorenz, B.; Kirmse, R.; Stach, J.; Beurskens, P. T.; Abram, U.; Münze, R. *J. Nucl. Med. Allied Sci.* **1989**, *33*, 291.
(6) Abram, U.; Kirmse, R.; Köhler, J.; Lorenz, B.; Kaden, L. *Inorg. Chim. Acta* **1987**, *129*, 15–20.
(7) Baldas, J.; Bonnyman, J.; Williams, G. A. *Aust. J. Chem.* **1984**, *37*, 751.
(8) Kaden, L.; Lorenz, B.; Kirmse, R.; Stach, J.; Abram, U. *Z. Chem.* **1985**, *25*, 29.
(9) Baldas, J.; Boas, J. F.; Bonnyman, J.; Williams, G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 2395–2400.
(10) Clarke, M. J.; Kastner, M. E.; Podbielski, L. A.; Fackler, P. H.; Schreifels, J.; Meinken, G.; Srivastava, S. C. *J. Am. Chem. Soc.* **1988**, *110*, 1818–1827.

0020-1669/90/1329-4123$02.50/0

Table II. Atomic Positions in *mer*-$[(SN)Cl_2(pic)_3Tc]\cdot CHCl_3$

atom	*x*	*y*	*z*
Tc	0.26621 (4)	0.76129 (6)	0.3065
Cl(1)	0.3089 (1)	0.5681 (2)	0.3229 (4)
Cl2	0.3735 (1)	0.8263 (3)	0.3892 (4)
Cl3	0.4307 (3)	0.4567 (5)	0.5552 (4)
Cl4	0.4931 (2)	0.5239 (4)	0.3380 (3)
Cl5	0.5221 (2)	0.6465 (6)	0.5483 (5)
S	0.1983 (2)	1.0134 (2)	0.3044 (5)
N1	0.2315 (4)	0.8945 (6)	0.303 (1)
N2	0.1771 (4)	0.6890 (7)	0.232 (1)
N3	0.3097 (5)	0.7716 (8)	0.134 (1)
N4	0.2236 (5)	0.7374 (8)	0.480 (1)
N4	0.2236 (5)	0.7374 (8)	0.480 (1)
C1	0.1796 (6)	0.608 (1)	0.149 (1)
C2	0.1228 (7)	0.555 (1)	0.104 (1)
C3	0.0581 (7)	0.582 (1)	0.143 (1)
C4	0.0550 (5)	0.670 (1)	0.229 (1)
C5	0.1134 (6)	0.720 (1)	0.269 (1)
C6	−0.0040 (9)	0.526 (1)	0.098 (2)
C7	0.1957 (7)	0.640 (1)	0.516 (1)
C8	0.1648 (7)	0.622 (1)	0.622 (1)
C9	0.1585 (7)	0.709 (1)	0.701 (1)
C10	0.1863 (7)	0.809 (1)	0.667 (1)
C11	0.2194 (7)	0.823 (1)	0.556 (1)
C12	0.1256 (9)	0.698 (2)	0.818 (2)
C13	0.3692 (6)	0.721 (1)	0.107 (1)
C14	0.3930 (6)	0.722 (1)	−0.005 (1)
C15	0.3660 (7)	0.776 (1)	−0.095 (1)
C16	0.3057 (8)	0.830 (1)	−0.067 (1)
C17	0.2792 (6)	0.826 (1)	0.048 (2)
C18	0.394 (1)	0.779 (1)	−0.221 (2)
C19	0.4583 (6)	0.572 (1)	0.473 (1)

determined on KBr pellets in a Nicolet Model 510 FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Varian 300 XL Fourier transform spectrometer. FAB mass spectral analyses were performed at the MIT Mass Spectrometry Facility.

Electrochemical measurements were performed by cyclic or square-wave voltammetry in 0.1 M tetraethylammonium perchlorate (TEAP) in DMF on a versatile electrochemical apparatus constructed in this laboratory.[11] A carbon-paste or platinum-button working electrode, Ag/AgCl reference electrode and platinum-wire auxiliary electrode were used in all measurements. Reduction potentials were determined as the peak potential in square-wave voltammetric scans and by the average of the anodic and cathodic peak potentials from cyclic voltammetric scans. All potentials were internally referenced against the ferrocene couple (400 mV vs NHE).[12]

Crystal Structure Determination. A dark green single crystal of *mer*-$[(SN)Cl_2(pic)_3Tc]\cdot CHCl_3$ was mounted on a glass fiber, which was placed in the beam of a Rigaku AFC5R diffractometer. Pertinent crystal data are given in Table I. Space group assignment was based on the systematic absences of $0kl$; $k + l \neq 2n$, and $h0l$; $h \neq 2n$. Intensities of three representative reflections, which were measured after every 150 reflections, remained constant throughout data collection so that no decay correction was necessary. An empirical absorption correction, based on azimuthal scans of several reflections, was applied. The Tc atom was located by direct methods and the structure solved from difference Fourier maps.[13,14] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions (C–H = 0.95 Å), and were assigned isotropic thermal parameters, which were 20% greater than the B_{equiv} value of the atom to which they were bonded. Refinement was by full-matrix least squares. Neutral-atom scattering factors[15] and anomalous dispersion effects were included in F_c;[16] the values for $\Delta f'$ $\Delta f''$ were those of Cromer.[12,17] Enantiomers were checked for polar dispersion error,[18] and the solution with the lower R value is reported.

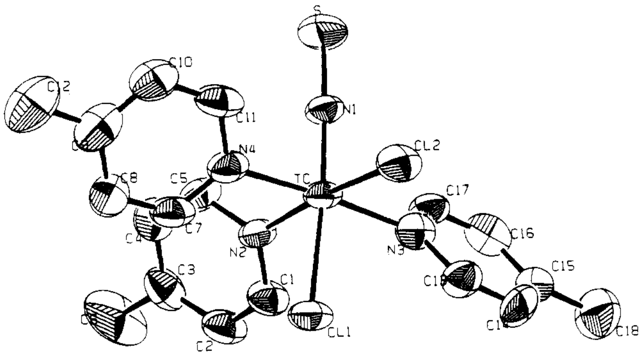

Figure 1. ORTEP[28] diagram of *mer*-$[Cl_3(pic)_3Tc]$. Hydrogens have been removed for clarity.

Table III. Selected Bond Distances (Å) in *mer*-$[(SN)Cl_2(pic)_3Tc]\cdot CHCl_3$

Tc–N1	1.73 (1)	Tc–Cl	2.443 (1)
Tc–N2	2.129 (6)	Tc–Cl2	2.430 (2)
Tc–N3	2.14 (1)	S–N1	1.54 (1)
Tc–N4	2.15 (2)		

Table IV. Bond Angles (deg) Surrounding the Tc atom in *mer*-$[(SN)Cl_2(pic)_3Tc]\cdot CHCl_3$

Cl1–Tc–Cl2	88.4 (1)	Cl2–Tc–N4	91.9 (3)
Cl1–Tc–N1	176.2 (4)	N1–Tc–N2	92.0 (4)
Cl1–Tc–N2	86.2 (2)	N1–Tc–N3	94.0 (5)
Cl1–Tc–N3	89.2 (3)	N1–Tc–N4	89.8 (6)
Cl1–Tc–N4	86.8 (3)	N2–Tc–N3	89.5 (4)
Cl2–Tc–N1	93.5 (3)	N2–Tc–N4	88.9 (4)
Cl2–Tc–N2	174.4 (2)	N3–Tc–N4	175.9 (4)
Cl2–Tc–N3	89.3 (3)	Tc–N1–S	176.0 (1)

Results

Compound Characterization. The small magnetic moments of bulk samples of these compounds indicate a small amount of paramagnetism, which may arise from temperature independent paramagnetism or result from thermal population of low-lying antibonding molecular orbitals. The reduction potentials of the pyridine, picoline, and lutidine complexes in DMF are 734 ± 7, 686 ± 8, and 714 ± 6 mV, respectively. Reversible couples were indicated for all three by cyclic voltammetric anodic and cathodic peak ratios close to unity and peak separations similar to that of the ferrocene internal standard.

Structure. An ORTEP diagram of *mer*-$[(SN)Cl_2(pic)_3Tc]\cdot CHCl_3$ is shown in Figure 1. Table II contains the atomic coordinates of the atoms in the asymmetric unit. Bond distances and angles surrounding the essentially octahedral technetium atom are listed in Tables III and IV. The Tc is displaced by 0.096 Å toward N1 out of the basal plane defined by Cl2, N2, N3, and N4. Owing to the 35–45° pitch of the pyridine rings, which can be tilted in either direction, the compound exists as enantiomers that are related by a crystallographic glide plane.

Discussion

In previous reports of thionitrosyls prepared by S atom donation to coordinated nitrides, sulfur, sulfur halides,[4] KSCN,[19] or propylene sulfide[20] has been used. For example, $[Cl_3(SN)(OPMe_2Ph)(PMe_2Ph)Tc^{II}]$ and $[Cl_2(SN)(PMe_2Ph)_3Tc^I]$ are made by reaction of $[NCl_2(PMe_2Ph)_2Tc]$ with an excess or an equivalent amount of S_2Cl_2, respectively,[6] and $[Cl_2(SN)(et_2dtc)_2Tc^{III}]$ is similarly fashioned from $[N(et_2dtc)_2Tc]$, where et$_2$dtc = diethyldithiocarbamate.[7] Dithionite provides a relatively inexpensive

---

(11) Clarke, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 5068–5075.

(12) Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854–2855. Gennett, T.; Milner, D. F.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 2787–2794.

(13) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42–46.

(14) Beurskens, P. T. DIRDIF. Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, Nijmegen, The Netherlands.

(15) Cromer, D. T.; Weber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2 A and 2.3.1.

(16) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(17) All calculations were performed using the TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985.

(18) Cotton, F. A.; Foxman, B. M. *Inorg. Chem.* **1968**, *7*, 1784–1792.

(19) Wright, M. J.; Griffith, W. P. *Transition Met. Chem. (Weinheim, Ger.)*, **1982**, *7*, 53.

(20) Bevan, P. C.; Chatt, J.; Dilworth, J. R.; Henderson, R. A.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1982**, 821–824.

means of donating the sulfur, while at the same time allowing higher oxidation state metal–nitrido cores to be used. Since dithionite is in equilibrium with $SO_2^{\cdot -}$, which is a good one-electron reductant, it is likely that the Tc^{VI} starting material is reduced in a single electron process to the corresponding Tc^{V} complex before undergoing a four-electron reduction upon addition of the sulfur atom to the nitrido ligand. The driving force for the atom-transfer process is undoubtedly the strong π-bonding interaction between Tc^{I} and the resulting thionitrosonium ligand.

The resulting $Tc—N{\equiv}S$ core is nearly linear with a bond angle of 176 (1)°, which is similar to the average of 176 (3)° for eight other thionitrosyl complexes.[21] The Tc–NS distance of 1.73 (1) Å is 0.41 Å shorter than the typical Tc–N length of 2.14 (1) Å exhibited by the $Tc–N_{pic}$ bonds, but is similar to the average Tc^{III}–NS bond of 1.75 Å in $[Cl_2(et_2dtc)_2(SN)Tc]$.[7] This marked bond shortening suggests substantial double-bond character between the Tc^{I} and the thionitrosyl and implies that the amount of double-bond character is similar in the technetium(III) complex. The higher coordination number and presence of four anionic ligands in the latter should compensate for the increased formal charge on the metal, thereby rendering a similar degree of back-bonding to the thionitrosyl. The $N{\equiv}S$ bond length of 1.54 (1) Å in *mer*-$[Cl_2(pic)_3(SN)Tc]$ is comparable to the average of 1.53 (3) Å for other coordinated thionitrosyls.[21] The displacement of the Tc out of the basal plane toward N1 also suggests substantial π-bonding in this direction. Taken together, the bonding parameters in the present complex indicate that the thionitrosyl is coordinated as $N{\equiv}S^+$ with extensive back-bonding from Tc^{I}.

In $[Br_2(CH_3NC)_3(ON)Tc^{I}]$[22] and $[(NH_3)_4(H_2O)(ON)Tc^{I}]Cl_2$[23,24] the nitrosyl exhibits a significant trans influence by lengthening the opposite bond by 0.055 and 0.15 Å, respectively. In the pentagonal-bipyramidal thionitrosyl complex $[Cl_2(et_2dtc)_2(SN)Tc^{III}]$,[7] the thionitrosyl causes an average lengthening between the cis and trans chlorides of 0.065 Å, while there is no trans influence in the technetium(II) compound $[Cl_3(Me_2PhP)(Me_2PhPO)(SN)Tc]$. In *mer*-$[Cl_2(pic)_3(SN)Tc]$, the axial Tc–Cl bond distance is only 0.013 Å longer than the equatorial Tc–Cl bond. These results imply that the trans influence exerted by thionitrosyl may be weaker than that of nitrosyl, but also that the magnitude of this effect can be strongly modulated by the donor/acceptor abilities of the other ligands.

While not exerting as strong a trans effect, thionitrosyl seems to be very nearly as good as nitrosyl in delocalizing electron density from the metal ion. From the Lever equation[25]

$$E^\circ = S_M \sum_{i=1}^{n} a_i E_{L(i)} - I_M$$

where n is the coordination number, a_i is the dentacity of a given ligand, E_L is the electrochemical parameter for the ligand, and the estimated electrochemical parameters for $Tc^{II,I}$ ($S_M = 1.4$, $I_M = -2.1$),[26] together with the reduction potential for $[(NO)(NH_3)_4(H_2O)Tc]Cl_2$ ($E^\circ = 800$ mV), an estimate of 1.80 for the E_L of $N{\equiv}O^+$ can be obtained. Similarly, an estimate of E_L for $N{\equiv}S^+$ of 1.77 can be derived from the E°'s for *mer*-$[(SN)Cl_2(pic)_3Tc]$ and related complexes. Consequently, $N{\equiv}S^+$ appears to be nearly as good as $N{\equiv}O^+$ at stabilizing Tc^{I} relative to Tc^{II}. This is consistent with the essentially linear Tc–NY bonds generally obtained, with Y being either O or S, and the similarity between the Tc^{I}–NS bond distance (1.732 Å) in *mer*-$[(SN)Cl_2(pic)_3Tc]$ and the average Tc^{I}–NO bond length of 1.72 Å.[22,23]

On the basis of photoelectron measurements, $N{\equiv}S^+$ is thought to be both a better π-donor and a better π-acceptor than $N{\equiv}O^+$.[27] The replacement of O by S results in a weaker π-bond to nitrogen because of poorer π-orbital overlap. Consequently, the π*-acceptor orbital is lower in energy and more able to interact favorably with filled metal d_π orbitals. A similar argument is made for the π-donor properties of $N{\equiv}S^+$ versus $N{\equiv}O^+$. Also, the lower electronegativity of sulfur relative to oxygen results in a higher negative charge on the nitrogen, enabling it to be a better σ-donor. The result of these interactions is that $N{\equiv}S^+$ may actually delocalize slightly more electron density from the metal, so that, despite the lower electronegativity of sulfur, $N{\equiv}S^+$ is approximately as effective as $N{\equiv}O^+$ in increasing the reduction potential of the $Tc^{II,I}$ couple.

Acknowledgment. We thank Professor Martha Teeter for providing excellent X-ray and computer facilities, which were funded by Boston College and NSF Grant BBS-8617930, and Professor Bruce Foxman (Brandeis University) for helpful discussions. We thank C. Zeng and C. E. Costello of the NIH region Mass Spectroscopies Facility (Grant NIH RR00317) at MIT for providing the mass spectra. This work was supported by NSF Grant CHE-8618011.

Supplementary Material Available: Listings of temperature factors for non-hydrogen atoms, bond distances and angles, and least-squares planes for *mer*-$[Cl_3(pic)_3Tc]\cdot CHCl_3$ (8 pages); a listing of calculated and observed and structure factor amplitudes for *mer*-$[Cl_3(pic)_3Tc]\cdot CHCl_3$ (10 pages). Ordering information is given on any current masthead page.

---

(21) Hauck, H. G.; Willing, W.; Mueller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1985**, *534*, 77–84 and references therein.

(22) Linder, K. E.; Davison, A.; Dewan, J. I.; Costello, C. E.; Maleknija, S. *Inorg. Chem.* **1986**, *25*, 2085.

(23) Armstrong, R. A. Chemistry of Tc in Low Oxidation States. Ph.D. Thesis, Stanford University, 1975.

(24) Armstrong, R.; Taube, H. *Inorg. Chem.* **1976**, *15*, 1904.

(25) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271–1285.

(26) Lu, J.; Clarke, M. J. *Inorg. Chem.*, in press.

(27) Lichtenberger, D. L.; Hubbard, J. L. *Inorg. Chem.* **1985**, *24*, 3835–3841.

(28) Johnson, C. K. ORTEPII. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.