Modulation of Tc–NX (X = O or S) Bonds by π-Acceptor Ligands†

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Transfer of a sulfur atom from S_2Cl_2 to *cis*-[TcN(Cl)(phen)$_2$]PF$_6$ (phen = 1,10-phenanthroline) yields *cis*-[Tc(NS)Cl(phen)$_2$]PF$_6$, which crystallizes in the triclinic space group, $P\bar{1}$ (no. 2), with cell parameters a = 9.850(3), b = 16.293(3), c = 8.349(2) Å, α = 100.06(2), β = 93.84(3) and γ = 106.96(3)°. The Tc–NS bond length is 1.782(6) Å and the N≡S distance is 1.538(6) Å with a Tc–N–S bond angle of 170.0(4)°. Reaction of $(NH_4)_2TcCl_6$ or NH_4TcO_4 with hydroxylamine hydrochloride in the presence of 1,10-phenanthroline yields *cis*-[Tc(NO)(NH$_3$)(phen)$_2$]$^{2+}$. The compound *cis*-[Tc(NO)(NH$_3$)(phen)$_2$][PF$_6$]$_2$·Me$_2$CO crystallizes in the triclinic space group, $P\bar{1}$ (no. 2), with a = 11.12(1), b = 14.25(6), c = 10.79(2) Å, α = 90.4(2), β = 107.9(1) and γ = 86.0(2)°. The Tc–NO bond length is 1.739(9) Å and the N≡O distance is 1.160(9) Å with a Tc–N–O bond angle of 171.9(8)°. Bond length and electrochemical data between series of complexes containing the [Tc–NX]$^{2+}$ (X = O or S) core indicate the effect of other π-acceptor ligands to be greater on thionitrosyl co-ordination.

Often subtle ligand modifications or reaction conditions give rise to significantly different technetium complexes through steric effects altering geometries or electronic effects inducing changes in oxidation states.[1,2] The products of atom-transfer reactions involving technetium are similarly sensitive to changes in the technetium co-ordination sphere and the atom donor/acceptor.[1,3] This is especially important in the synthetic chemistry of this element, since many syntheses begin with the removal of oxygen from $[TcO_4]^-$ or an oxotechnetium(V) core. Recently, atom transfer to co-ordinated nitride has also become synthetically useful.[4,5]

Thionitrosyl complexes of transition metals can be prepared by the transfer of S atoms from S_8, S_2Cl_2 and even dithionite to nitrido ligands resulting in a four-electron reduction of the metal centre.[6–9] By contrast, a convenient synthetic route to isoelectronic technetium nitrosyl complexes has been the reduction of $(NH_4)_2TcCl_6$ with hydroxylamine hydrochloride, which serves both as a reductant and a source of NO$^+$, resulting in a synthetic intermediate, $[Tc(NO)Cl_x(H_2O)_y]^{(3-x)+}$, in which the chloro ligands are readily substituted.[10] In this report we present the synthesis of *cis*-[Tc(SN)Cl(phen)$_2$]PF$_6$ from *cis*-[TcN(Cl)(phen)$_2$]Cl and compare the structure of the thionitrosyl complex with a similar nitrosyl species, *cis*-[Tc(NO)(NH$_3$)(phen)$_2$]$^{2+}$, prepared from $(NH_4)_2TcCl_6$ in the presence of 1,10-phenanthroline (phen) and (NH$_3$OH)Cl.

Complete neglect of differential overlap (CNDO/2) calculations and simple electronegativity considerations indicate that the σ-donor orbital of NS is at higher energy than that of NO, while the π*-acceptor orbital of NS is at lower energy than the analogous orbital of NO. Also there is weaker π bonding in NS relative to NO. This has been taken to indicate that NS may be both a better σ donor and π acceptor than NO leading to the suggestion that for some metal ions NS relative to NO binding may (1) be stronger, (2) exert a stronger *trans* effect, and (3) be more effective in delocalizing electron density from the metal.[11–13] This is complicated by sulfur's ability to π-donate and its lower electronegativity allowing the nitrogen to accumulate electron density.[14] Moreover, in the complexes *trans*-[Os(NX)Cl$_3$(PPh$_3$)$_2$], NS appears to be a weaker π acceptor than is NO.[15]

Experimental

Syntheses.—The compound *cis*-[Tc(NS)Cl(phen)$_2$]PF$_6$·H$_2$O was prepared by refluxing [TcN(Cl)(phen)$_2$]Cl·H$_2$O[16] (60 mg) with S_2Cl_2 (200 μl) in chloroform (50 cm^3) for 2 h. After cooling, a dark brown solid was filtered off and washed with chloroform and diethyl ether. This material was dissolved in water (20 cm^3), filtered, and a few drops of half-saturated aqueous NH_4PF_6 added to induce precipitation of an amorphous brown solid. Yield: 90% (Found: C, 39.45; H, 2.40; Cl, 5.05; N, 9.75. Calc. for $C_{24}H_{18}ClF_6N_5OPSTc$: C, 40.95; H, 2.60; Cl, 5.05; N, 9.95%). Crystals without the water of hydration were obtained by solvent evaporation from acetone, acetone–water (1:2) or acetonitrile. IR in KBr pellet (cm^{-1}): 1426s, 1173vs, [ν(N=S)], 842vs, 723s and 555s, [ν(P–F)]. UV/VIS in acetonitrile, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 267 (6.75 × 10^4), 358(sh), 464 (7050), and 667 (800). Reduction potentials were determined by square-wave voltammetry in 0.1 mol dm^{-3} tetraethylammonium perchlorate in dimethylformamide (dmf): 0.89 ± 0.01 (Tc^{II}–Tc^{I}, reversible) and − 1.09 V (phen reduction, irreversible).

The compound *cis*-[Tc(NO)(NH$_3$)(phen)$_2$][PF$_6$]$_2$ was prepared by dissolving $(NH_4)_2TcCl_6$[17] (90 mg) or an equimolar amount of NH_4TcO_4 in water (20 cm^3) containing (NH$_3$OH)Cl (374 mg) and 1,10-phenanthroline (234 mg). After boiling for 2 h with stirring the resulting purple-brown solution was filtered to remove a small amount of purple solid. A concentrated aqueous solution of NH_4PF_6 was added to induce precipitation of a brown solid, which was dissolved in acetone–water (1:2) and loaded onto a CM-25 Sephadex ion-exchange column. The column was developed with 0.05 mol dm^{-3} ammonium formate followed by 0.2 mol dm^{-3} ammonium formate, which eluted the product. Concentrated NH_4PF_6 was added to the eluted band to precipitate a brown solid, which was collected by filtration and washed with ice-cold water and diethyl ether before storage in a vacuum desiccator. Yield from $(NH_4)_2TcCl_6$, 76%; from $(NH_4)TcO_4$, 93% (Found: C, 36.45; H, 2.50; N, 10.30. Calc. for $C_{24}H_{19}F_{12}N_6OP_2Tc$: C, 36.20; H, 2.40; N, 10.55%). IR in KBr pellet (cm^{-1}): 1715vs, [ν(N=O)], 1630m, [ν(C=N)], 1602m, [ν(C=N)], 1581m [ν(C=N)], 1518m, 1433s, 1152m, 843vs, 723s, and 554s [ν(P–F)]. UV/VIS in acetonitrile, λ_{max}/nm (ε/dm^{-3} mol^{-1} cm^{-1}): 271 (2.35 × 10^4), 348(sh), 448 (4620), 475(sh) and 548(sh). Crystals of *cis*-[Tc(NO)(NH$_3$)(phen)$_2$][PF$_6$]$_2$·Me$_2$CO were obtained by the slow evaporation of a saturated solution of the complex in acetone–water (1:1) at room temperature. This

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† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Reduction potentials (*vs.* NHE) of *cis*-$[Tc(NO)(NH_3)(phen)_2]^{2+}$ and *cis*-$[Tc(NS)Cl(phen)_2]^+$ at $I = 0.1$ mol dm^{-3}

Complex	E_1/V	E_2/V	Ref.
cis-$[Tc(NO)(NH_3)(phen)_2]^{2+}$	1.01 ± 0.01^a	-0.98^b	This work
trans-$[Tc(NO)(H_2O)(NH_3)_4]^{2+}$	0.80^c		10
cis-$[Tc(NS)Cl(phen)_2]^+$	0.89 ± 0.01^b	-1.09^b	This work
mer-$[Tc(NS)Cl_2(py)_3]$	0.73^b		4

[a] MeCN, 0.1 mol dm^{-3} NEt_4ClO_4. [b] dmf, 0.1 mol dm^{-3} NEt_4ClO_4. [c] Water.

compound (dissolved in acetone for spotting) exhibited an R_f of 0.62 on a silica gel TLC plate developed with 30% MeCN in $CHCl_3$.

Compound Characterization.—Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Magnetic susceptibility studies were performed on a Cahn model 7500 electrobalance equipped with a 14 502 G (1.45 T) permanent magnet at 25 °C. Proton NMR spectra were recorded on a Varian 300 XL Fourier-transform spectrometer, solid-state IR spectra on Nujol emulsions, KBr or CsBr disks with a Nicolet model 510 FT-IR spectrophotometer, and UV/VIS spectra on a Cary model 2400 spectrometer.

Electrochemical measurements were performed by cyclic or square-wave voltammetry in 0.1 mol dm^{-3} tetraethylammonium perchlorate in dmf or acetonitrile on a versatile electrochemical apparatus constructed in this laboratory. A gold 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. All potentials were internally referenced against the ferrocene couple [400 mV *vs.* normal hydrogen electrode (NHE)].[18]

Structure Analysis and Refinement.—A brown single crystal of *cis*-$[Tc(NO)(NH_3)(phen)_2][PF_6]_2{\cdot}Me_2CO$ was obtained by dissolving *cis*-$[Tc(NO)(NH_3)(phen)_2][PF_6]_2$ in acetone–water and allowing the solvent to evaporate, and was then mounted on a glass fibre.

Crystal data. $C_{27}H_{25}F_{12}N_6O_2P_2Tc$, $M = 854.37$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.12(1)$, $b = 14.25(6)$, $c = 10.79(2)$ Å, $\alpha = 90.4(2)$, $\beta = 107.9(1)$, $\gamma = 86.0(2)°$, $U = 1622(6)$ Å^3 (by least-squares refinement on diffractometer angles for 35 automatically centred reflections, $\lambda = 1.541\ 78$ Å), $Z = 2$, $D_c = 1.749$ g cm^{-3}, $F(000) = 852$. Crystal dimensions: $0.40 \times 0.20 \times 0.50$ mm, μ(Cu-Kα) = 55.32 cm^{-1}.

Data collection and processing. Rigaku AFC5R diffractometer at 20(1) °C, ω–2θ scan mode with ω scan width = 0.88 + 0.30 tanθ, ω scan rate = 32° min^{-1}, $2\theta_{max} = 120.1°$, Cu-Kα radiation; 4809 unique observations, 3880 observed reflections with $I > 3\sigma(I)$. An empirical absorption correction, based on azimuthal scans of several reflections, was applied with relative transmission factors 0.55–1.0. Intensities of three representative reflections, which were measured after every 150 reflections, remained constant throughout data collection, so that no decay correction was necessary.

Structure analysis and refinement. Direct methods (Tc and P atoms) followed by Fourier difference methods.[19–21] Full-matrix, least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions (C–H 0.95 Å), which were assigned isotropic thermal parameters 20% greater than the B_{equiv} value of the atoms to which they were bonded. Neutral atom scattering factors[22] and anomalous dispersion effects were included in F_{calc};[23] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[22] Minimization of the function $\Sigma w(|F_o| - |F_c|)^2$, with the weighting scheme $w = 4(F_o)^2[\sigma^2/(F_o)^2]^2$, gave final R and R' values of 0.065 and 0.084 with 451 variables. Goodness of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{\frac{1}{2}} = 2.49$.

A dark brown single crystal of *cis*-$[Tc(NS)Cl(phen)_2]PF_6$ was obtained upon solvent evaporation of an acetonitrile solution of the monohydrate compound. Data collection and solution of the structure proceeded similarly to that described above.*

Crystal data. $C_{24}H_{16}ClF_6N_5PSTc$, $M = 685.81$, triclinic, space group $P\bar{1}$, $a = 9.850(3)$, $b = 16.293(3)$, $c = 8.349(2)$ Å, $\alpha = 100.06(2)$, $\beta = 93.84(3)$, $\gamma = 106.96(3)°$; $U = 1251.9(5)$ Å^3, $Z = 2$, $D_c = 1.819$ g cm^{-3}, $F(000) = 680$. Crystal dimensions: $0.50 \times 0.43 \times 0.30$ mm, μ(Cu-Kα) = 55.32 cm^{-1}.

Data collection and processing. ω Scan width = 1.47 + 0.30 tanθ, $2\theta_{max} = 118.7°$, 3636 unique observations, 3513 observed, absorption correction with relative transmission factors 0.73–1.0.

Structure analysis and refinement. Direct methods (Tc, Cl and P atoms) followed by Fourier difference methods;[19–21] R and R' values of 0.044 and 0.064 with 361 variables, goodness of fit = 3.29.

Additional material for both structures available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results

Synthesis and Characterization.—The complex *cis*-$[Tc(NO)(NH_3)(phen)_2]^{2+}$ was conveniently synthesised by modifying the method for preparing *trans*-$[Tc(NO)(H_2O)(NH_3)_4]^{2+}$,[10,24] so as to have an additional strong ligand (phen) present at modest concentration (0.065 mol dm^{-3}). Since a similar method has been reported to yield *cis*-$[Tc(NO)Cl(phen)_2]^+$,[25] the possibility that this complex occurs as a significant product in the synthesis was investigated by both spectroscopy and TLC to determine that the crude product of the reaction between $(NH_3OH)Cl$ and NH_4TcO_4 was, in fact, $[Tc(NO)(NH_3)(phen)_2]^+$. Consequently, *cis*-$[Tc(NO)Cl(phen)_2]^+$ is *not* produced as an intermediate, which is later substituted in chromatographic purification by the ammonia present in the ion-exchange eluent.

An analogous method of preparing thionitrosyl complexes is not available; however, advantage can be taken of the ability of nitrido ligands to accept other atoms in atom-transfer redox reactions. Consequently, S-atom transfer to *cis*-$[TcN(Cl)(phen)_2]^+$ to yield *cis*-$[Tc(NS)Cl(phen)_2]^+$ was readily accomplished with S_2Cl_2 in chloroform.

Reduction potentials for the two complexes are listed in Table 1. Both exhibited a reversible couple in the anodic region, which is assigned to a Tc^{II}–Tc^{I} couple. These couples yielded square-wave peak currents and shapes nearly identical with that of equimolar ferrocene in the same solution. Both technetium complexes also exhibited a larger, irreversible, reduction wave around −1.0 V, which is attributed to the reduction of a phenanthroline ligand followed by decomposition of the complex.

Structures.—The structures of *cis*-$[Tc(NO)(NH_3)(phen)_2]^+$ and *cis*-$[Tc(NS)Cl(phen)_2]^+$ are shown in Figs. 1 and 2, respectively. Atomic positions for *cis*-$[Tc(NO)(NH_3)(phen)_2][PF_6]_2{\cdot}MeCO$ and *cis*-$[Tc(NS)Cl(phen)_2]PF_6$ are listed in Table 2 and 3, respectively. Bond distances around the Tc in

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* In this case, however, a Fourier difference map indicated the presence of enantiomeric disorder involving the chloride and thionitrosyl groups. Atoms N(1′) S′ and Cl′ were placed in calculated positions for the opposite enantiomer and the solution refined isotropically with their B-values constrained to equal those of the original atoms and the total of each enantiomeric atom pair constrained to unity. After convergence, the populations were set at 85 and 15% for the original and minority disordered atoms, respectively, and the original atoms refined anisotropically.

Table 2 Atomic positions in *cis*-$[Tc(NO)(NH_3)(phen)_2][PF_6]_2\cdot Me_2CO$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Tc	0.294 31(6)	0.171 25(5)	0.180 10(6)	C(3)	0.374(1)	0.438(1)	−0.059(1)
P(1)	0.066 3(3)	0.255 7(2)	0.675 0(2)	C(4)	0.293(1)	0.447 9(8)	0.019(1)
P(2)	0.787 4(3)	0.175 0(2)	0.101 3(3)	C(5)	0.227(1)	0.535 6(8)	0.035(1)
F(1)	0.023 1(8)	0.200 2(5)	0.544 3(6)	C(6)	0.153(1)	0.539 6(8)	0.112(1)
F(2)	0.142 5(8)	0.165 4(5)	0.747 3(7)	C(7)	0.136(1)	0.458 1(7)	0.179(1)
F(3)	0.106 9(7)	0.311 1(5)	0.807 2(6)	C(8)	0.056(1)	0.459 4(8)	0.258(1)
F(4)	−0.010(1)	0.344 9(6)	0.601 5(7)	C(9)	0.049(1)	0.379 7(8)	0.321(1)
F(5)	0.183 7(8)	0.282 1(7)	0.636 9(9)	C(10)	0.117 2(8)	0.297 2(7)	0.307 9(8)
F(6)	−0.050 0(7)	0.226 1(7)	0.712 6(8)	C(11)	0.200 7(8)	0.373 8(6)	0.168 4(8)
F(7)	0.732 8(6)	0.268 7(5)	0.151 9(7)	C(12)	0.279 4(8)	0.366 7(7)	0.084 3(8)
F(8)	0.886 3(6)	0.236 4(5)	0.066 3(9)	C(13)	0.556 0(8)	0.229 8(6)	0.361(1)
F(9)	0.845 1(8)	0.084 4(5)	0.049(1)	C(14)	0.650 8(9)	0.231 8(8)	0.481(1)
F(10)	0.690 7(7)	0.118 3(5)	0.143 2(9)	C(15)	0.637 8(9)	0.193 3(7)	0.590(1)
F(11)	0.691 9(7)	0.196 4(7)	−0.034 7(7)	C(16)	0.527 4(8)	0.148 6(6)	0.582 9(9)
F(12)	0.885 4(9)	0.155 6(7)	0.243(1)	C(17)	0.503(1)	0.106 3(8)	0.689(1)
O(1)	0.414 7(7)	0.032 5(6)	0.051 5(8)	C(18)	0.398(1)	0.058 5(8)	0.675(1)
O(2)	0.526 5(8)	0.463 5(7)	0.300 4(9)	C(19)	0.308 4(9)	0.049 9(6)	0.548 5(9)
N(1)	0.370 4(7)	0.084 5(6)	0.111 2(8)	C(20)	0.202(1)	−0.001 9(7)	0.527(1)
N(2)	0.336 2(6)	0.281 1(5)	0.074 4(7)	C(21)	0.122(1)	−0.009 1(7)	0.404(1)
N(3)	0.193 4(6)	0.293 2(5)	0.231 1(6)	C(22)	0.146 5(9)	0.035 4(7)	0.302(1)
N(4)	0.449 1(6)	0.186 7(5)	0.349 9(6)	C(23)	0.327 4(7)	0.092 2(5)	0.442 5(7)
N(5)	0.247 1(6)	0.087 7(5)	0.318 0(7)	C(24)	0.438 0(8)	0.145 6(6)	0.459 1(8)
N(6)	0.119 9(6)	0.156 6(5)	0.021 8(6)	C(25)	0.589(2)	0.590(1)	0.440(2)
C(1)	0.411 9(9)	0.273 5(8)	−0.003(1)	C(26)	0.612(1)	0.504 2(9)	0.371(1)
C(2)	0.430(1)	0.353(1)	−0.070(1)	C(27)	0.747(1)	0.469(1)	0.392(1)

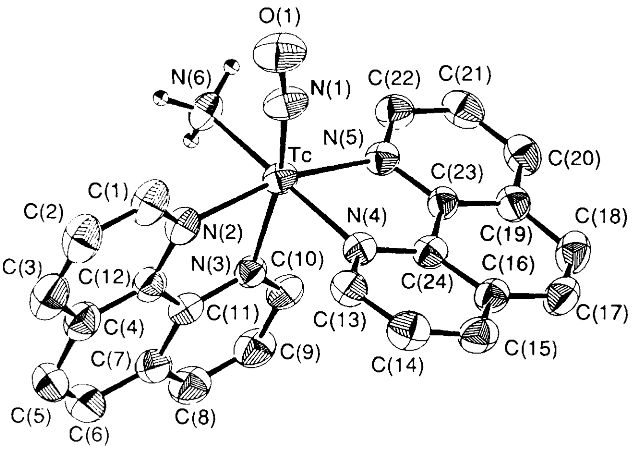

Fig. 1 An ORTEP[26] diagram of *cis*-$[Tc(NO)(NH_3)(phen)_2]^{2+}$ Thermal ellipsoids at 40% probability

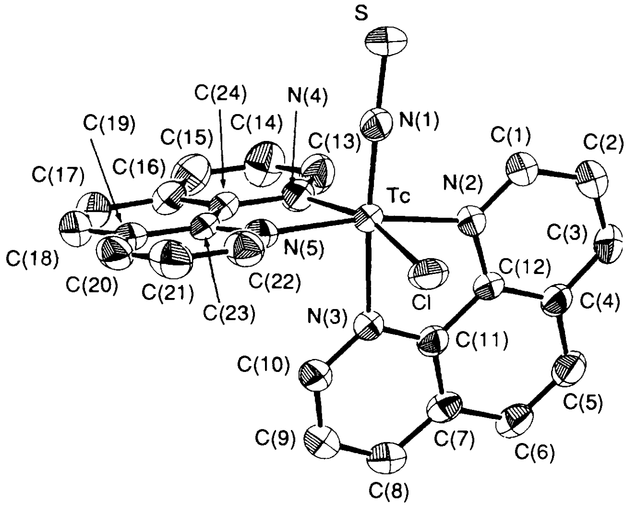

Fig. 2 An ORTEP[26] diagram of *cis*-$[Tc(NS)Cl(phen)_2]^+$. Thermal ellipsoids at 50% probability

both complex ions are summarized in Table 4, while bond angles are given in Table 5.

Discussion

Nitrosyl Complex.—While a synthesis of $[Tc(NO)(NH_3)(phen)_2]^+$ starting from $(NH_4)_2TcCl_6$ but with the addition of the phenanthroline after reduction with hydroxylamine was reported by Armstrong and Taube,[10,27] their product was not fully characterized and yielded variable elemental analyses. A preparation similar to the one devised here starting from NH_4TcO_4 has been reported to yield *cis*-$[Tc(NO)Cl(phen)_2]^+$.[25] The reaction product is important, since *cis*-$[Tc(NO)Cl(phen)_2]^+$ should serve as a good synthetic intermediate owing to the facile substitution of chloride on $[Tc^I\text{–}NO]^{2+}$ cores by nitrogen ligands. On the other hand, since nitrogen ligands on this core are often exceptionally stable, $[Tc(NO)(NH_3)(phen)_2]^+$ is not likely to lead to new series of complexes.

Fig. 1 shows that the product occurring in high yields from either starting material under the reaction conditions given herein is *cis*-$[Tc(NO)(NH_3)(phen)_2]^+$, which is consistent with the earlier observation that the ammonia present from the starting materials (or possibly impurities or products of hydroxylamine) successfully competes with chloride for sites on the $[Tc^I\text{–}NO]^{2+}$ core.[10,27] Close correspondence in the UV/VIS and IR spectra and $Tc^{II}\text{–}Tc^I$ reduction potentials as measured by cyclic voltammetry indicates that this complex and that reported by Armstrong and Taube[10,27] are the same. Relative to NO• and NO^+, ν(N=O) is lowered by 125 and 435 cm^{-1}, respectively, upon co-ordination by Tc^I.

Consistent with substantial back bonding to the phenanthrolines in the nitrosyl complex, the average equatorial $Tc\text{–}N_{phen}$ bond distance is 2.11 ± 0.01 Å, which is 0.075 Å shorter than the $Tc\text{–}NH_3$ bond length. In addition to the short Tc–NO bond distance (Table 4), strong retrodative bonding to the nitrosyl group is indicated by the 0.167 Å displacement of the Tc out of the plane defined by the equatorial nitrogens, and the lengthening of the axial $Tc\text{–}N_{phen}$ distance by 0.05 Å relative to the equatorial N_{phen}. Owing to the competition for d_π orbitals between the phenanthrolines and the nitrosyl, the Tc–NO

Table 3 Atomic positions in *cis*-$[\mathrm{Tc(NS)Cl(phen)_2}]\mathrm{PF_6}$

Atom	x	y	z
Tc	0.360 83(4)	0.260 01(2)	0.071 68(4)
Cl	0.313 5(2)	0.389 1(1)	0.019 7(2)
Cl′	0.368(1)	0.173 7(7)	−0.170(1)
S	0.393 7(2)	0.155 8(1)	−0.293 8(2)
S′	0.258(1)	0.425 8(8)	−0.015(1)
N(1)	0.366 6(6)	0.206 3(3)	−0.131 7(7)
N(1′)	0.309(3)	0.343(2)	0.019(4)
N(2)	0.580 9(4)	0.333 3(2)	0.108 4(5)
N(3)	0.397 1(4)	0.321 7(2)	0.330 9(4)
N(4)	0.372 1(4)	0.150 6(3)	0.173 1(5)
N(5)	0.142 2(4)	0.194 6(3)	0.081 4(5)
C(1)	0.670 5(6)	0.338 7(3)	−0.004 8(7)
C(2)	0.809 8(6)	0.395 9(4)	0.027 7(8)
C(3)	0.858 4(5)	0.447 2(3)	0.180 3(7)
C(4)	0.768 1(5)	0.442 9(3)	0.301 8(6)
C(5)	0.811 1(5)	0.493 0(3)	0.465 1(7)
C(6)	0.719 8(5)	0.483 0(3)	0.542 3(6)
C(7)	0.577 8(5)	0.423 2(3)	0.542 8(6)
C(8)	0.479 0(5)	0.409 6(3)	0.655 3(6)
C(9)	0.344 6(6)	0.353 5(3)	0.606 2(6)
C(10)	0.306 5(5)	0.312 5(3)	0.442 7(6)
C(11)	0.532 8(5)	0.376 8(3)	0.380 8(6)
C(12)	0.630 6(5)	0.385 0(3)	0.260 2(5)
C(13)	0.487 7(5)	0.127 9(3)	0.213 1(7)
C(14)	0.479 1(6)	0.055 7(4)	0.284 3(8)
C(15)	0.350 2(6)	0.004 7(3)	0.313 1(7)
C(16)	0.226 6(6)	0.027 0(3)	0.273 9(6)
C(17)	0.084 4(6)	−0.021 6(3)	0.298 7(7)
C(18)	−0.029 1(6)	0.000 3(3)	0.251 7(7)
C(19)	−0.017 0(5)	0.072 8(3)	0.173 4(6)
C(20)	−0.133 1(5)	0.096 7(4)	0.115 4(7)
C(21)	−0.109 2(6)	0.166 5(4)	0.043 8(7)
C(22)	0.029 8(5)	0.215 2(4)	0.026 1(6)
C(23)	0.118 9(5)	0.122 9(3)	0.151 1(5)
C(24)	0.241 6(5)	0.099 7(3)	0.200 4(5)
P	0.865 8(1)	0.251 51(8)	0.557 5(2)
F(1)	0.798 5(5)	0.154 2(2)	0.445 1(5)
F(2)	0.810 5(5)	0.217 5(3)	0.714 1(5)
F(3)	1.006 1(4)	0.228 4(3)	0.598 7(9)
F(4)	0.932 5(6)	0.347 4(3)	0.660 8(6)
F(5)	0.930 8(7)	0.284 2(3)	0.406 7(6)
F(6)	0.727 6(6)	0.271 8(4)	0.514(1)

Table 4 Bond distances (Å) surrounding the Tc atom in *cis*-$[\mathrm{Tc(NO)(NH_3)(phen)_2}][\mathrm{PF_6}]_2\cdot\mathrm{MeCO}$ and the major enantiomer of *cis*-$[\mathrm{Tc(NS)Cl(phen)_2}]\mathrm{PF_6}$

	$[\mathrm{Tc(NO)(NH_3)(phen)_2}]^{2+}$	$[\mathrm{Tc(NS)Cl(phen)_2}]^{+}$
Tc–N(1)	1.739(9)	1.782(6)
Tc–N(2)	2.10(1)	2.119(4)
Tc–N(3)	2.16(1)	2.179(4)
Tc–N(4)	2.115(7)	2.130(4)
Tc–N(5)	2.122(8)	2.120(4)
Tc–N(6)	2.175(8)	
Tc–Cl		2.387(2)
O(1)–N(1)	1.160(9)	
S–N(1)		1.538(6)

Table 5 Bond angles (°) surrounding the Tc atom in *cis*-$[\mathrm{Tc(NO)(NH_3)(phen)_2}]^{2+}$ and *cis*-$[\mathrm{Tc(NS)Cl(phen)_2}]^{+}$

	$[\mathrm{Tc(NO)(NH_3)(phen)_2}]^{2+}$	$[\mathrm{Tc(NS)Cl(phen)_2}]^{+}$
N(1)–Tc–N(2)	93.7(4)	94.0(2)
N(1)–Tc–N(3)	169.1(3)	168.0(2)
N(1)–Tc–N(4)	95.9(4)	93.0(2)
N(1)–Tc–N(5)	99.4(4)	96.2(2)
N(1)–Tc–N(6)	89.6(4)	
N(2)–Tc–N(3)	76.8(4)	76.8(1)
N(2)–Tc–N(4)	95.5(3)	99.5(1)
N(2)–Tc–N(5)	165.8(3)	169.6(1)
N(2)–Tc–N(6)	88.9(3)	
N(3)–Tc–N(4)	90.4(3)	81.0(1)
N(3)–Tc–N(5)	90.5(4)	92.8(1)
N(3)–Tc–N(6)	84.9(3)	
N(4)–Tc–N(5)	78.0(3)	77.9(2)
N(4)–Tc–N(6)	172.7(2)	
N(5)–Tc–N(6)	96.3(3)	
Cl–Tc–N(1)		100.6(2)
Cl–Tc–N(2)		87.2(1)
Cl–Tc–N(3)		86.9(1)
Cl–Tc–N(4)		164.4(1)
Cl–Tc–N(5)		93.0(1)
Tc–N(1)–O(1)	171.9(8)	
Tc–N(1)–S		170.0(4)

distance is longer than in *trans*-$[\mathrm{Tc(NO)(H_2O)(NH_3)_4}]^{2+}$ (1.716 Å), in which there is no such competition, and $[\mathrm{TcBr_2(NO)(CNCMe_3)_3}]$ (1.726 Å),[28] in which the π-withdrawing effect of the isonitriles is partially negated by the two bromo ligands. Similar logic applies to the 0.04 Å decrease in the N≡O bond distance between *trans*-$[\mathrm{Tc(NO)(H_2O)(NH_3)_4}]^{2+}$ and *cis*-$[\mathrm{Tc(NO)(NH_3)(phen)_2}]^{2+}$.

Owing to the similar sizes of the chloro and amine ligands and the identity of the phenanthroline ligands, the degree of distortion from octahedral around the technetium atoms in both complexes (*cf.* Table 5) is quite similar. The slight Tc–N–X (X = O or S) bending evident in both complexes (*cf.* Table 5) is also similar, but represents a significantly higher degree than in other complexes with the $[\mathrm{Tc{-}NX}]^{2+}$ core.[10,28]

Sulfur-atom Transfer.—While sulfur-atom transfer from dithionite to $[\mathrm{TcNCl_4}]^-$ in 2-methylpyridine (2Me-py) solution yields, *mer*-$[\mathrm{Tc(NS)Cl_2(2Me\text{-}py)_3}]$,[4] a similar reaction did not occur with *cis*-$[\mathrm{TcN(Cl)(phen)_2}]^+$ in dmf, MeCN, or ethanol. Nevertheless, S-atom transfer was possible in $\mathrm{CHCl_3}$, $\mathrm{CH_2Cl_2}$ and methanol with $\mathrm{S_2Cl_2}$ as the donor. The resulting Tc–N≡S core is slightly bent (see Table 5) with a bond angle similar to the average of 175(4)° for six other thionitrosyl complexes.[4,9] The Tc–NS distance (see Table 4) is 0.34 Å shorter than the typical Tc–N length of 2.213(6) Å exhibited by the equatorial $\mathrm{Tc{-}N_{phen}}$ bonds, which is consistent with significant π bonding between the metal and the thionitrosyl. While significantly longer than the $\mathrm{Tc^{I}}$–NS bonds of 1.73(1) Å in *mer*-$[\mathrm{Tc(NS)Cl_2(2Me\text{-}py)_3}]$[4] and 1.75 Å in *mer*-$[\mathrm{Tc(NS)Cl_2(PMe_2Ph)_3}]$.[29] Significant π bonding is also substantiated by the thionitrosyl stretching frequency (1173 $\mathrm{cm^{-1}}$) which is closer to that of $\mathrm{SN^{\bullet}}$ (1205 $\mathrm{cm^{-1}}$) than that for $\mathrm{SN^+}$ (1437 $\mathrm{cm^{-1}}$), while being close to the average for four other thionitrosyl complexes (1200 $\mathrm{cm^{-1}}$).[30]

The displacement of the Tc by 0.033 Å out of the basal plane toward N(1) also suggests significant π bonding in this direction, and the N≡S bond length of 1.538(6) Å in *cis*-$[\mathrm{Tc(NS)Cl(phen)_2}]^+$ is similar to the average of 1.53(5) Å for other co-ordinated thionitrosyls.[4,9] Taken together, the bonding parameters and ν(N≡S) indicates that the thionitrosyl is co-ordinated as $\mathrm{N{\equiv}S^+}$ with appreciable back bonding from $\mathrm{Tc^{I}}$. On the same basis, however, the retrodative bonding to the thionitrosyl is less than in other thionitrosonium complexes, which can likely be attributed to the competition for d_π electron density generated by the phenanthroline ligands.

The Tc–N bond *trans* to the thionitrosyl ligand is 0.056 Å longer than the average of those to the equatorial nitrogens. In the pentagonal-bipyramidal thionitrosyl complex $[\mathrm{Tc^{III}(NS)Cl_2(S_2CNEt_2)_2}]$[5] the thionitrosyl causes an average lengthening

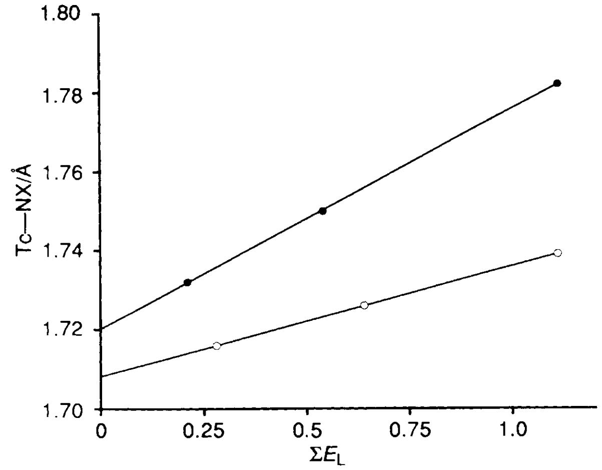

Fig. 3 Plot of Tc-NX [X = O (◇) or S (◆)] bond lengths *versus* ΣE_L for the non-nitrosyl ligands. Data taken from refs. 4, 10, 28, 29 and this work

between the *cis* and *trans* chlorides of 0.065 Å, while there is no *trans* influence evident in $[Tc^{II}(NS)Cl_3(PMe_2Ph)(PMe_2PhO)]$.[7] In *mer*-$[Tc^{I}(NS)Cl_2(2Me\text{-}py)_3]$, the axial Tc–Cl bond distance is only 0.013 Å longer than the equatorial Tc–Cl bond.[4] While these results imply that the *trans* influence exerted by thionitrosyl may be modulated by the donor/acceptor abilities of the other ligands, the available data set is too small to extract a clear trend and the rigidity of the phenanthroline chelate in the present case may cause an apparently larger *trans* influence.

Electrochemistry.—An estimate of the electrochemical parameter E_L for the nitrosyl ligand of 1.11 is obtained from the Lever equation,[31] by using the estimated electrochemical parameters for Tc^{II}–Tc^{I} (S_M = 1.4, I_M = −2.0)[32] and the Tc^{II}–Tc^{I} reduction potential for *cis*-$[Tc(NO)(NH_3)(phen)_2]^+$ (Table 1). A similar estimate for the thionitrosyl yields a value of 1.33. These values are substantially lower than the previous estimates of ≈1.8 for both ligands, which may be due to their being somewhat bent in these complexes with concomitant changes in hybridization and π-acceptor abilities, or to the presence of other strong π-acceptor ligands decreasing the effectiveness of the retrodative bonding to the nitrosyl groups relative to other technetium(I) thionitrosyl complexes.[4]

A correlation might also be expected between the sum of the Lever electrochemical parameters, which increase as an empirical function of the net electron-acceptor properties of a ligand, and the ability of the Tc^{I} to backbond to the nitrosyl as reflected in the Tc–NX (X = O or S) bond distance. Such a correlation is evident in Fig. 3 which plots ΣE_L for the non-nitrosyl ligands in two series of technetium(I) nitrosyl and thionitrosyl complexes *versus* the pertinent bond length. This plot clearly shows an increase in the Tc–NX bond length with increasing competition for π-electron density exerted by the non-nitrosyl ligands.

Conclusion

In comparison to other complexes containing the $[Tc^{I}\text{–}NS]^{2+}$ core,[4,29] the Tc–NS bond is relatively long. The much longer Tc–NX and smaller N=X bonds, the smaller displacement of Tc from the basal plane, and the diminished effect on the $N\equiv X^+$ stretching frequency for X = S relative to O suggest weaker Tc–NS π back bonding, despite the expectation of enhanced π back bonding to NS^+ when a chloro rather than an amine ligand is present. The slightly greater E_L for NS relative to NO may be due to less σ donation rather than greater π back bonding. While the greater *trans* influence in the thionitrosyl complex is at odds with this, the difference is not quite significant on a 2σ basis. Overall for these technetium(I) complexes it appears that thionitrosyl binds less strongly than nitrosyl. The excellent linear correlations shown in Fig. 3 between Tc–NX bond lengths and ΣE_L [slopes and intercepts, respectively, are 0.0277(1) Å/E_L and 1.708(1) Å for the nitrosyl and 0.0556(2) Å/E_L and 1.720(1) Å for the thionitrosyl complexes] indicates that the net availability of π density on the metal allowed by the other ligands has a greater effect on thionitrosyl co-ordination. This may be a direct consequence of the lower electronegativity and greater polarizability of S relative to O and offers at least a partial explanation of why NS has been variously thought to be the stronger π acceptor in complexes such as $[Os(NX)Cl_5]^{2-}$ but a weaker π acceptor in complexes such as $[Os(NX)Cl_3(PPh_3)_2]$.[11,15] In addition to their value in predicting bond lengths, these correlations may also be useful in correlating reactivities of the $[Tc\text{–}NX]^{2+}$ core.

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