

Note

The synthesis and characterization of a cationic technetium nitrosyl complex: The X-ray crystal structure of $[\text{TcCl}(\text{NO})(\text{DPPE})_2](\text{PF}_6) \cdot \text{CH}_2\text{Cl}_2$

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Abstract

The reaction of the ammonium pertechnetate with a stoichiometric excess of hydroxylamine hydrochloride in methanol yields a nitrosyl containing intermediate which can subsequently be reacted with reducing ligands to form nitrosyl complexes in various oxidation states. The reaction with a sixfold excess of diphenyl-phosphinoethane (DPPE) yields the Tc(I) cation $[\text{TcCl}(\text{NO})(\text{DPPE})_2]^+$ which can be precipitated cleanly with tetraphenylborate. The infrared spectrum displays an absorption at 1728 cm^{-1} which corresponds to the nitrosyl group. The ESI(+) mass spectrum displays the parent ion $[\text{TcCl}(\text{NO})(\text{DPPE})_2]^+$ as the only signal at 960 m/z .

The X-ray crystal structure of the hexafluorophosphate salt shows a mutually *trans* arrangement of the nitrosyl and chloride ligands with the two bidentate phosphine ligands coordinated in the equatorial plane. The nitrosyl and chloride ligands display the usual site disorder which makes discussion of bond lengths tenuous. However, the Tc–N–O bond angle of $179.0(2)^\circ$ reflects the sp hybridization of the nitrosyl nitrogen atom. The Tc–P bonds are somewhat elongated at 2.3810(6), 2.3947(6), 2.4096(5) and 2.4321(6) Å, due to the steric congestion around the metal ion. The Tc–Cl bond is unexceptional at 2.3262(7) Å. The coordination geometry of this complex is best described as a distorted octahedron.

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1. Introduction

The nitrosyl core, in its more common linear bonding mode, consists of a metal ion which is doubly bonded to a nitrogen atom, which in turn is doubly bonded to an oxygen atom. In its bent conformation, the nitrogen atom is singly bonded to the metal ion which results in a lone pair of electrons residing on the sp^2 hybridized nitrogen. The oxygen atom is sp^2 hybridized with two lone pairs of electrons in both conformations (see Fig. 1).

Most of the technetium nitrosyl chemistry reported to date has evolved from the anionic starting material $[\text{Bu}_4\text{N}][\text{Tc}(\text{NO})\text{Cl}_4]$ [1–6]. The preparation of this precursor involves reacting $[\text{Bu}_4\text{N}][\text{TcOCl}_4]$ with hydroxylamine hydrochloride and crystallizing the analytically pure product overnight.

2. Experimental

Caution! Technetium-99 is a weak β^- -emitter ($E = 0.292\text{ MeV}$, $t_{1/2} = 2.12 \times 10^5\text{ years}$). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere [7]. Reagents and solvents were used as received

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unless otherwise stated. Routine infrared spectra were obtained on a Perkin–Elmer spectrum one FTIR spectrometer. Analytical results were obtained from Atlantic Micro-lab Inc., Norcross, GA. Mass spectra were recorded on a Bruker Daltonics APEXII 3 Tesla Fourier transform mass spectrometer (ion cyclotron resonance mass spectrometer).

X-ray crystallographic data collection parameters:

The crystal data and some experimental details of the structure determination are given in Table 1.

A orange prismatic crystal of complex **1** was isolated from the $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{Et}_2\text{O}$ mixture as described below. The crystals dimensions were $0.20 \times 0.18 \times 0.08$ mm. The diffractometer employed was a Siemens platform goniometer with a CCD detector with the data set collected at $100(2)^\circ$. The scan mode used was $2\theta/\omega$, with a maximum 2θ of 60° . A total of 13679 reflections were collected of which 13084 were of $I > 2\sigma(I)$ and were used in the final refinement. The technetium atom was located using the direct methods. The chlorine atom is disordered against the nitrosyl group at 85:15 ratio with the ratio refined freely. The Flack-x parameter [8] refined to a non-zero value. Therefore, the structure was refined as a racemic twin (twin law $-1000 -1000 -1$). The twin ratio was refined freely and converged at 0.617(16). This makes it impossible to derive a conclusion about the absolute structure from the value of the Flack parameter. Neutral atomic scattering factors were used throughout the analysis. Extinction effects were not observed. Final hydrogen atom positions were calculated. All non-hydrogen atoms were refined anisotropically.

3. Synthesis

$[\text{TcCl}(\text{NO})(\text{DPPE})_2](\text{PF}_6) \cdot \text{CH}_2\text{Cl}_2$. A 1 mL sample of $(\text{NH}_4)[\text{TcO}_4]$ (0.35 M) was evaporated to dryness. To this was added a fivefold excess of hydroxylamine hydrochloride dissolved in 50 mL MeOH. The reaction mixture was brought to reflux and heated for 45 min giving a red-

brown solution. To this was added 6 equiv. of diphenylphosphinoethane (DPPE). This solution was refluxed for an additional 45 min. To this was added 1 equiv. of ammonium hexafluorophosphate. The solution was evaporated to dryness, and the resulting red oil was dissolved in methylene chloride and then layered with methanol and diethyl ether. This solution gave red-brown/green dichroic crystals after 24 h at room temperature. Yield: 373 mg (93%).

Analytical results for crude $[\text{TcCl}(\text{NO})(\text{DPPE})_2](\text{PF}_6) \cdot \text{CH}_2\text{Cl}_2$: calculated for $[\text{TcCl}_3\text{P}_5\text{F}_6\text{ONC}_{53}\text{H}_{50}]$: C, 53.44; H, 4.23; N, 1.18; Cl, 8.93. Found: C, 53.57; H, 4.22; N, 1.04; Cl, 8.96%.

IR(KBr): $\nu(\text{Tc}=\text{N})$, 1098 cm^{-1} ; $\nu(\text{N}=\text{O})$, 1723 cm^{-1} .

ESI(+) mass spectrum: $960 m/z$, $[\text{TcCl}(\text{NO})(\text{DPPE})_2]^+$.

4. Discussion

Hydroxylamine, like the organohydrazines, is a redox active reagent which tends to push electrons into high oxidation state transition metals, causing the metal to be reduced, while forming a multiply bonded, metal-nitrosyl core. This process is referred to as reductive nitrosylation and was first reported with rhenium in 1982 [9]. In this report, we employ the process to synthesize a nitrosyl containing intermediate which can be employed to generate the cationic complex $\text{H}[\text{Tc}(\text{NO})\text{Cl}_4]$, the most commonly employed of the technetium-nitrosyl precursors. The other frequently employed synthon is the Tc(II) complex $[\text{TcCl}_3(\text{NO})(\text{PPh}_3)_2]$, which is synthesized from $(\text{Bu}_4\text{N})[\text{Tc}(\text{NO})\text{Cl}_4]$. Since the established preparation of $(\text{Bu}_4\text{N})[\text{Tc}(\text{NO})\text{Cl}_4]$ requires a full day to synthesize and isolate, we set out to develop a quicker preparation that might also be utilized at the tracer level to synthesize the complex from the short-lived (6 h) isotope $[\text{m}^{99}\text{TcO}_4]^-$ which is employed in biological assays.

A fivefold excess of hydroxylamine hydrochloride reacts with ammonium pertechnetate in refluxing methanol to give a red-brown nitrosyl containing intermediate. By adding a sixfold stoichiometric excess of diphenylphosphinoethane (DPPE) to the intermediate, we were able to synthesize the cationic, octahedral complex $[\text{TcCl}(\text{NO})(\text{DPPE})_2]^+$, which can be cleanly precipitated from solution as the tetraphenylborate salt. The infrared spectrum of this complex displays a prominent absorption at 1728 cm^{-1} , which is attributed to the nitrosyl ligand. The ESI(+) mass spectrum displays a single peak at $960 m/z$ which corresponds to the parent cation (see Fig. 2).

Table 1
X-ray data for structure determination of complex **1**

Empirical formula	$\text{C}_{53}\text{H}_{50}\text{Cl}_3\text{F}_6\text{NOP}_5\text{Tc}$
Formula weight	1190.14
Crystal system	orthorhombic
Space group	$Pns2(1)$
a (Å)	21.559(3)
b (Å)	11.3660(12)
c (Å)	19.083(2)
V (Å ³)	4676.0(10)
Space group	$Pna2(1)$
Z	4
D_{calc} (Mg/m ³)	1.691
μ (mm ⁻¹)	0.719
Radiation (λ , Å) ^a	Mo $K\alpha$ (0.71073)
Temperature (K)	100
T_{max} , T_{min}	0.8695, 0.9447
R , R_w	0.0311, 0.0721
Goodness-of-fit	1.046

^a Graphite monochromated.

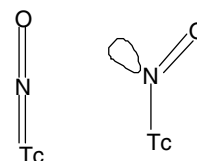


Fig. 1. Nitrosyl bonding conformations, linear on the left and bent on the right.

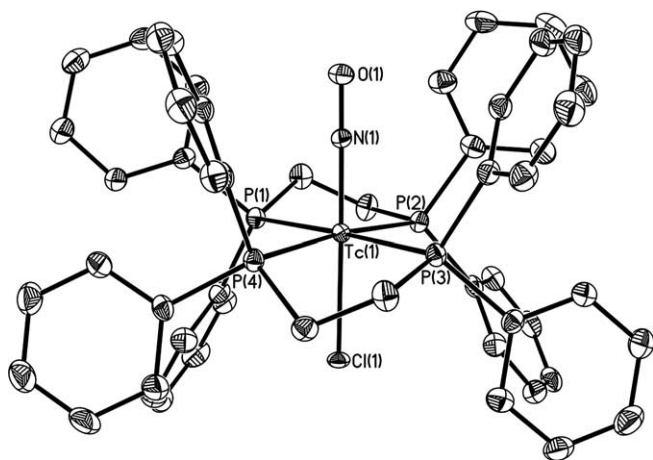


Fig. 2. The ORTEP diagram for the cationic complex $[\text{TcCl}(\text{NO})(\text{DPPE})_2]^+$ with the carbon atoms unlabelled for visual clarity. The PF_6 anion and solvate molecule have also been omitted.

Table 2
Selected bond lengths (Å) and angles (°) for $[\text{TcCl}(\text{NO})(\text{DPPE})_2](\text{PF}_6)$

Tc(1)–N(1)	1.717(3)
Tc(1)–Cl(1)	2.3262(7)
Tc(1)–P(1)	2.3947(6)
Tc(1)–P(2)	2.4096(5)
Tc(1)–P(3)	2.4321(6)
Tc(1)–P(4)	2.3810(6)
N(1)–O(1)	1.145(3)
N–Tc(1)–Cl(1)	178.08(7)
N–Tc(1)–P(3)	91.63(7)
Cl(1)–Tc(1)–P(3)	87.71(2)
N–Tc(1)–P(1)	90.08(7)
P(1)–Tc(1)–Cl(1)	90.54(2)
P(3)–Tc(1)–P(1)	177.972(19)
N–Tc(1)–P(2)	92.03(7)
P(2)–Tc(1)–Cl(1)	89.87(2)
P(2)–Tc(1)–P(3)	100.00(2)
N–Tc(1)–P(2)	92.03(7)
P(2)–Tc(1)–Cl(1)	89.87(2)
P(2)–Tc(1)–P(1)	81.018(19)
P(4)–Tc(1)–N	93.96(7)
Cl(1)–Tc(1)–P(4)	84.15(2)
P(3)–Tc(1)–P(4)	80.351(19)
P(1)–Tc(1)–P(4)	98.46(2)
P(2)–Tc(1)–P(4)	173.991(19)
O–N(1)–Tc(1)	179.0(2)

By substituting sodium hexafluorophosphate for the sodium tetraphenylborate in the preparation, X-ray quality crystals of the complex can be grown from dichloromethane layered with methanol and diethylether. The complex displays octahedral coordination geometry with the nitrosyl and chloride ligands in the axial positions. The Tc–N bond length is 1.717(3) Å and the N–O bond length is 1.145(3) Å which both fall in the range expected for linear nitrosyl ligands. The Tc–N–O bond angle is 179.0(2)° which reflects the sp hybridization of the nitrogen atom. The Tc–Cl bond is 2.3262(7) Å which is unexceptional for bonds of this type. (The distances and the angle refer to the major component of the disordered atoms.) X-ray crystallographic determina-

tions for this type of complex, with a nitrosyl ligand in the position *trans* to a chloride ligand frequently result in disorder problems. In this instance, there was an 85:15% site disorder for these axial ligands. This makes any in depth analysis of the bonding parameters of the axial ligands problematic, we can state that the atoms involved are in a linear bonding mode and that there is nothing in the crystallography or chemistry to make us suspect any unusual bond lengths in either of the mutually *trans* ligands. The four Tc–P bond lengths are between 2.3810(6) and 2.4321(6) Å, which are in the expected range for these type bonds. There is severe steric congestion around the equatorial plane imposed by the two bulky bidentate phosphine ligands. The *cis* P–Tc–P bond angles range from 80.35(2)° to 100.00(2)° and the Cl–Tc–P bonds range from 84.15(2)° to 90.54(2)°. See Fig. 2 which displays an ORTEP for the cation $[\text{TcCl}(\text{NO})(\text{DPPE})_2]^+$ (see Table 2).

5. Conclusion

We have developed a new synthetic route to useful technetium nitrosyl complexes which are generated in a 90 min preparation starting from pertechnetate. This protocol should allow syntheses at the tracer level employing the short-lived isotope $^{99\text{m}}\text{Tc}$, which is used in biological assays. We are currently examining the versatility of this preparative route to see which oxidation states can be accessed from the reactive nitrosyl containing intermediate employing different coligands.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.09.053.

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