Inorg. Chem. **2006**, *45*, 6589–6591

Inorganic Chemistry
Communication

Technetium Complexes with Triazacyclononane

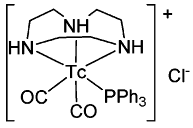
Henrik Braband and Ulrich Abram*

*Institute of Chemistry and Biochemistry, Freie Universität Berlin, Fabeckstrasse 34−36,
D-14195 Berlin, Germany*

Received April 4, 2006

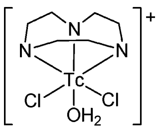
$[NBu_4][TcOCl_4]$ reacts with ethylene glycol and 1,4,7-triazacyclononane (tacn) in MeOH under the formation of the deep-blue oxotechnetium(V) cation $[TcO(OC_2H_4O)(tacn)]^+$, which can readily be oxidized by air to give the stable technetium(VII) compound $[TcO_3(tacn)]^+$. The reaction with aqueous HCl results in reduction and the formation of the cationic technetium(III) complex $[TcCl_2(OH_2)(tacn)]Cl$. The products were isolated in crystalline form and studied spectroscopically and by X-ray diffraction.

Despite the fact that the coordination chemistry of rhenium with tripodal ligand systems derived from 1,4,7-trithiacyclononane (9S3) and 1,4,7-triazacyclononane (tacn) is well explored,[1−3] there are only a few reports on structurally well-characterized technetium complexes with these ligands. The technetium(I) tricarbonyl complex $[Tc(CO)_3(9S3)]^+$ is remarkably stable and even resists heating in 1 M HNO_3 or 3% H_2O_2 solutions; rapid oxidation and formation of TcO_4^- was observed under more rigid conditions (heating in 30% H_2O_2).[4] This behavior is unlike that of the rhenium analogue, which can be converted to $[ReO_3(9S3)]^+$ under mild conditions. Attempts to prepare the analogous $[TcO_3(9S3)]^+$ cation from pertechnetate, 9S3, and HBF_4 resulted in an instantaneous C−S bond cleavage and reduction of the metal. Complexes of the compositions $[Tc(9S3)_2]^{2+}$ and $[Tc(9S3)(SC_2H_5SC_2H_5S)]^+$ were isolated from such reactions.[1f,g] The technetium(I) complex $[Tc(CO)_2(PPh_3)_2(tacn)]^+$ (**I**) was isolated from the reaction of $[Tc(CO)_3Cl(PPh_3)_2]$ and the tripodal ligand in tetrahydrofuran (THF) and is hitherto the only structurally characterized representative of a technetium complex with tacn.[5]

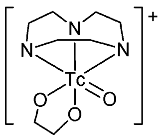


(I)

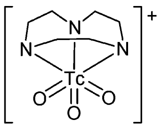
Here, we report on the syntheses and structures of the technetium tacn complexes $[TcCl_2(OH_2)(tacn)]Cl$, (**II**), $[TcO(OC_2H_4O)(tacn)]Br$ (**III**), and $[TcO_3(tacn)]Br$ (**IV**), which contain the metal in the formal oxidation states “3+”, “5+”, and “7+”.



(II)



(III)



(IV)

$[NBu_4][TcOCl_4]$ reacts with a mixture of ethylene glycol and tacn•3HCl in THF upon the addition of NEt_3 under the formation of the blue compound $[TcO(OC_2H_4O)(tacn)]Cl$.[6] Recrystallization was performed from an aqueous KBr solution. This procedure was adopted from the synthesis of the rhenium analogue and gives the bromide salt of the complex as large, bright-blue crystals. $[TcO(OC_2H_4O)(tacn)]$-

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* To whom correspondence should be addressed. E-mail: abram@chemie.fu-berlin.de.

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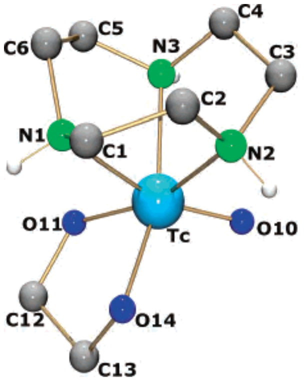

Figure 1. Molecular structure of the complex cation in $[TcO(OC_2H_4O)(tacn)]Br\cdot H_2O$.[8] Hydrogen atoms at carbon atoms are omitted for clarity.

Br readily dissolves in water but is only sparingly soluble in alcohols. The ^1H NMR spectrum of the compound is complex and is characterized by high-order multiplets due to the nonequivalent methylene protons. The IR spectrum shows the $\nu_{Tc=O}$ stretch at 949 cm^{-1}, and bands at 656 and 610 cm^{-1} can be assigned to the Tc−O vibration of the glycolato ligand.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in $[TcO(OC_2H_4O)(tacn)]^+$

Tc-O10	1.669(2)	Tc−O11	1.928(2)
Tc−O14	1.939(2)	Tc−N1	2.260(2)
Tc−N2	2.174(2)	Tc−N3	2.164(2)
O10−Tc−O11	111.9(1)	O10−Tc−O14	106.8(1)
O10−Tc−N1	160.3(1)	O10−Tc−N2	87.8(1)
O10−Tc−N3	92.7(1)	O11−Tc−O14	82.7(1)
O11−Tc−N1	85.0(1)	O11−Tc−N2	159.3(1)
O11−Tc−N3	92.3(1)	O14−Tc−N1	84.7(1)
O14−Tc−N2	98.0(1)	O14−Tc−N3	160.3(1)
N1−Tc−N2	74.6(1)	N1−Tc−N3	75.9(1)
N2−Tc−N3	80.1(1)		

$[TcO(OC_2H_4O)(tacn)]Br\cdot H_2O$ (**III**$Br\cdot H_2O$) crystallizes in the noncentrosymmetric space group $P2_1$.[7] The technetium atom is coordinated in a strongly distorted octahedral environment. Figure 1 shows the structure of the complex cation. Table 1 contains selected bond lengths and angles. Main distortions of the molecular structure are due to the restrictions with the tripodal ligand and the sterical bulk of the multiply bonded oxo oxygen. This results in small N−Tc−N angles and an extension of the O10−Tc−L_{equ} angles. The strong structural trans influence of the oxo ligand causes a Tc−N1 bond, which is by approximately 0.1 Å longer than the Tc−N2 and Tc−N3 bonds. Hydrogen bonds between the nitrogen atoms of the tacn ligands and the bromide counterions form a two-dimensional network. Details are given in Table S1 and Figure S1 of the Supporting Information.

$[TcO(OC_2H_4O)(tacn)]Br$ is stable as a solid. Aqueous solutions of the complex, however, slowly decompose under the formation of the technetium(VII) cation $[TcO_3(tacn)]^+$ (**IV**). This conversion even occurs at room temperature after the addition of a drop of diluted acid and can be detected by a change of color from blue to yellow and the release of ethylene glycol. Yellow crystals of $[TcO_3(tacn)]Br$ can be isolated upon removal of the solvent.[9] The product is perfectly stable against air and water. It is only sparingly soluble in organic solvents but can readily be recrystallized from water. The $\nu_{Tc=O}$ stretching vibration is observed at 891 cm^{-1}. The ^{99}Tc NMR spectrum shows a broad resonance (line width ≈ 2500 Hz) at 359 ppm (vs TcO_4^-), which is in the same range as has been observed earlier for a series of technetiumVII) trioxo complexes.[10]

The reactivity of oxotechnetium(VII) and oxorhenium(V) complexes with ethylene glycolato ligands was carefully studied by Pearlstein and Davison at complexes of the type $[MOCl(OC_2H_4O)(L)]$ (M = Re, Tc; L = bipyridine and phenanthroline derivatives).[11] Thermolysis of such rhenium complexes results in ethylene abstraction and the formation of $[ReO_3(L)]$ complexes, while the reverse reaction, a [3 + 2] addition of alkenes ($CHR^1{=}CHR^2$) to $[TcO_3(L)]$ and the subsequent interconversion to glycolato ligands in $[TcOCl(OCHR^1CHR^2O)(L)]$ complexes, dominates in the corresponding technetium system. The resulting glycolates can be released by the addition of concentrated HCl, which results in the formation of $[TcOCl_3(L)]$.

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(6) $[TcO(OC_2H_4O)(tacn)]Br\cdot H_2O$ (**III**$Br\cdot H_2O$): $[NBu_4][TcOCl_4]$ (50 mg, 0.1 mmol) was dissolved in 2 mL of THF and added to a suspension of tacn·3HCl (48 mg, 0.2 mmol) and ethylene glycol (12 mg, 0.2 mmol) in 10 mL of THF. A total of 3 drops of NEt_3 was added, and the mixture was stirred for 3 h at room temperature. A gray-blue solid precipitated during this time. This solid was collected by fitration and recrystallized from an aqueous KBr solution as blue plates. Yield: 12 mg (30%). IR data (KBr, cm^{-1}): 3500 (m), 3082 (st), 2962 (w), 2835 (w), 1261 (m), 1114 (m), 1099 (m), 1049 (m), 991 (m), 949 (st), 903 (m), 868 (m), 833 (w), 806 (m), 656 (st), 610 (st), 525 (m), 451 (w). ^1H NMR (D_2O): δ 1.9−3.7 (m, 12H, CH_2 of tacn), 4.0−5.4 (m, 4H, CH_2 of glycolate) ppm.

(7) X-ray crystal structure calculations. $[TcO(OC_2H_4O)(tacn)]Br\cdot H_2O$: Bruker Smart CCD, $C_8H_{19}N_3O_4BrTc$, blue plates, monoclinic, space group $P2_1$, $a = 7.207(5)$ Å, $b = 13.442(5)$ Å, $c = 7.319(5)$ Å, $\beta = 113.74(1)°$, $V = 649.0(7)$ Å^3, $Z = 2$, $D_{calc} = 2.043$ g/cm^3, $\theta = 3.03−30.53°$, 8101 reflections collected, 3766 independent reflections, $\mu = 4.195$ mm^{-1} (SADABS, $T_{min} = 0.77487$, $T_{max} = 1.0000$), solved by direct methods and refined by full-matrix least-squares procedures using *SHELXS* and *SHELXL* (Sheldrick, G. M., University of Göttingen: Göttingen, Germany), 154 parameters, Flack 0.002(5); $R = 0.0211$, $wR = 0.0216$. $[TcO_3(tacn)]Br$: CAD4, $C_6H_{15}N_3O_3BrTc$, yellow block, hexagonal, space group $P6_3$, $a = 8.057(5)$ Å, $b = 8.057(5)$ Å, $c = 10, 805(5)$ Å, $V = 607(1)$ Å^3, $Z = 2$, $D_{calc} = 1.942$ g/cm^3, $\theta = 3.48−26.99°$, 1760 reflections collected, 896 independent reflections, $\mu = 4.463$ mm^{-1} (absorption correction: DELABS, $T_{min} = 0.325$, $T_{max} = 0.755$), solved by direct methods and refined by full-matrix least-squares procedures using *SHELXS* and *SHELXL* (Sheldrick, G. M., University of Göttingen: Göttingen, Germany), 48 parameters, Flack 0.012(3), $R = 0.0253$, $wR = 0.0381$. $[TcCl_2(OH_2)(tacn)]Cl$: CAD4, $C_6H_{17}N_3OCl_3Tc$, green plate, monoclinic, space group $P2_1/n$, $a = 12.841(3)$ Å, $b = 12.973(3)$ Å, $c = 7.801(1)$ Å, $\beta = 90.16(1)°$, $V = 1299.6(4)$ Å^3, $Z = 4$, $D_{calc} = 1.797$ g/cm^3, $\theta = 3.05−27.00°$, 2544 reflections collected, 1284 independent reflections, $\mu = 1.701$ mm^{-1} (no absorption correction), solved by direct methods and refined by full-matrix least-squares procedures using *SHELXS* and *SHELXL* (Sheldrick, G. M., University of Göttingen: Göttingen, Germany), 106 parameters, $R = 0.0637$, $wR = 0.1637$.

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(9) $[TcO_3(tacn)]Br$ (**IV**Br): $[TcO(OC_2H_4O)(tacn)]Br\cdot H_2O$ (20 mg, 0.05 mmol) was dissolved in 2 mL of water, and 1 drop of 0.1 M HCl was added. The color slowly changed from blue to yellow. The solution was concentrated in vacuum to about 0.5 mL. Yellow crystals deposited upon standing in a refrigerator. Yield: 13 mg (74%). IR data (KBr, cm^{-1}): 3036 (s), 2889 (w), 2851 (m), 2785 (w), 1489 (w), 1454 (m), 1385 (w), 1265 (w), 1165 (w), 1115 (m), 1072 (m), 995 (m), 891 (s), 845 (m), 814 (m), 629 (w), 598 (w), 529 (w), 436 (w). ^{99}Tc NMR (D_2O): 358 ppm (line width 2500 Hz).

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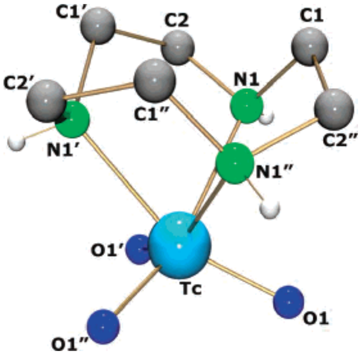

Figure 2. Molecular structure of the complex cation in $[TcO_3(tacn)]Br$.[8] Hydrogen atoms at carbon atoms are omitted for clarity. Bond lengths (Å) and angles (deg): Tc−N1 2.239(4), Tc−O1 1.703(4), N1−Tc−N1′ 73.9(2), N1−Tc−O1 88.5(2), N1−Tc−O1′ 86.1(2), N1−Tc−O1″ 156.2(2), O1−Tc−O1′ 106.5(2). Symmetry operations: prime, $1 - y, x - y, z$; double prime, $1 - x + y, 1 - x, z$.

A similar reaction of $[Tc^{V}O(OC_2H_4O)(tacn)]$ with 1 M HCl results in the reduction of the metal and the formation of the green technetium(III) complex $[TcCl_2(OH_2)(tacn)]Cl$ (**II**Cl),[12] while the oxidative hydrolysis of the technetium(V) complex and the immediate formation of $[Tc^{VII}O_3(tacn)]$-Br is observed when solutions of **III**Br are only slightly acidified.[9]

Figure 2 shows the molecular structure of cation **IV**.[7] The technetium atom is located on a 3-fold axis of the hexagonal space group $P6_3$. Two pairs of facially coordinated nitrogen and oxygen atoms produce a strongly distorted coordination octahedron. The Tc−O bonds are slightly longer than those to the terminal oxygen atoms in the molecular structure of Tc_2O_7.[13] The long Tc−N bonds of 2.239 Å reflect the structural trans influence of the oxo ligands. It is interesting to note that this influence is obviously stronger in the technetium(VII) compound under study than in the corresponding rhenium(VII) compound, in which the Re−N bonds are slightly shorter. The complex cations and the bromide counterions are connected by hydrogen bonds, which finally form a two-dimensional network. Details are given in Figure S2 and Table S2 of the Supporting Information.

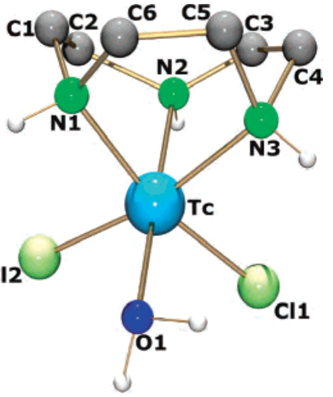

Figure 3. Molecular structure of the complex cation in $[TcCl_2(OH_2)(tacn)]$-Cl.[8] Hydrogen atom at carbon atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in $[TcCl_2(OH_2)(tacn)]Cl$

Tc−N1	2.13(2)	Tc−N2	2.10(3)
Tc−N3	2.13(2)	Tc−Cl1	2.317(5)
Tc−Cl2	2.269(7)	Tc−O1	2.29(2)
N1−Tc−N2	81.5(8)	N1−Tc−N3	78.4(6)
N1−Tc−Cl1	167.9(4)	N1−Tc−Cl2	92.5(5)
N1−Tc−O1	89.8(7)	N2−Tc−N3	78.1(8)
N2−Tc−Cl1	90.2(5)	N2−Tc−Cl2	93.9(7)
N2−Tc−O1	167.8(5)	N3−Tc−Cl1	91.4(5)
N3−Tc−Cl2	168.6(7)	N3−Tc−O1	91.7(8)
Cl1−Tc−Cl2	96.7(2)	Cl1−Tc−O1	97.0(4)
Cl2−Tc−O1	95.1(4)		

The molecular structure of the technetium(III) cation $[TcCl_2(OH_2)(tacn)]^+$ is shown in Figure 3. Selected bond lengths and angles are summarized in Table 2. The formation of a reduction product of **III**Br in 1 M HCl is not unexpected,[13] also in light of the fact that a similar reaction of the rhenium analogue, which finally gives $[ReCl_3(tacn)]$, requires more rigid conditions such as a HCl/zinc dust mixture.[2f] The bond lengths and angles in **II** are unexceptional. The technetium atom is coordinated in a distorted octahedral environment. The Tc−O bond is comparably long but in the range of coordinated water molecules.[14]

In summary, it can be stated that the coordination chemistry of technetium with tacn is similar to that of rhenium.[2] Main differences, however, are due to the different redox potentials of the two group 7 elements. Probably the most remarkable features of the presented technetium chemistry are the easy access and the high stability of the technetium(VII) trioxo complex. This recommends the hitherto relatively unappreciated $[TcO_3]^+$ core also for further studies with regard to nuclear medical applications. Corresponding studies are being currently undertaken in our laboratory.

Supporting Information Available: Illustration of the network of and hydrogen bonds for both $[TcO(OC_2H_4O)(tacn)]Br{\cdot}H_2O$ and $[TcO_3(tacn)]Br$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) $[TcCl_2(OH_2)(tacn)]Cl$ (**II**Cl): $[TcO(OC_2H_4O)(tacn)]Br$ (20 mg, 0.05 mmol) was dissolved in 4 mL of 1 M HCl and heated at reflux for 2 h. After concentration to about 0.5 mL and storage overnight in a refrigerator, green plates of **II**Cl precipitated. Yield: 9 mg (52%).

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