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High-Valent Technetium Complexes with the $[^{99}TcO_3]^+$ Core from in Situ Prepared Mixed Anhydrides of $[^{99}TcO_4]^-$ and Their Reactivities

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The highly reactive mixed anhydrides $[TcO_3(OCOPh)]$ and $[TcO_3(OBF_3)]^-$ were synthesized by treatment of $[TcO_4]^-$ with strong Lewis acids benzoyl chloride and $BF_3 \cdot OEt_2$. These mixed anhydrides, prepared in situ, were used as precursors for the synthesis of complexes containing the $[TcO_3]^+$ core. Subsequent reactions with bi- or tridentate ligands resulted in new complexes comprised of the $[TcO_3]^+$ core. As examples with bidentate ligands, the classical complexes $[TcO_3Cl(bipy)]$ (**1**) (bipy = 2,2′-bipyridine) and $[TcO_3Cl(phen)]$ (**2**) (phen = 1,10-phenanthroline) have been prepared by this strategy and structurally characterized. The new compounds $[TcO_3(bpza)]$ (**3**) (bpza = di-1*H*-pyrazol-1-ylacetate), $[TcO_3(bpza^*)]$ (**4**) (bpza* = bis(3,5-dimethyl-1*H*-pyrazol-1-yl)acetate), $[TcO_3(tpzm^*)]^+$ (**6**) (tpzm* = 1,1,1-methanetriyltris(3,5-dimethyl-1*H*-pyrazole), and $[ReO_3(tpzm^*)][ReO_4]$ (**7**) are examples of complexes with tripod ligands. The complexes have been structurally characterized, and their ^{99}Tc NMR spectra have been recorded. As a common feature, the X-ray structures show a distinct widening of the O–Tc–O angles, almost to a tetrahedral angle. With the perspective of radiopharmaceutical applications, water stability and reactivities toward alkenes are described.

Introduction

Coordination compounds or organometallic complexes of technetium in its highest oxidation state +VII are relatively rare.[1] This contrasts its higher homologue, rhenium, with which a relatively wide variety of high-valent complexes have been described in the literature.[2] This discrepancy can be understood as a consequence of the distinctly increased oxidation power of technetium vs rhenium in high oxidation states going along with reduced stabilities, higher reactivities, and more difficult accessibilities. Probably as important, however, is the lack of Tc_2O_7, an existing compound which can only be synthesized and handled in specialized laboratories, due to its volatility and very high water sensitivity.[3] Nevertheless, Tc_2O_7 served as a starting material for the synthesis of $H_3C{-}TcO_3$ and $Me_3SnO{-}TcO_3$.[4] On the other hand, Re_2O_7 is a very convenient starting material for the direct syntheses of complexes comprising the $[ReO_3]^+$ core and further ligands to complete the coordination sphere. In addition to Tc_2O_7, the volatile compound $(Me)_3SiO{-}TcO_3$ has been prepared directly from $Ag[TcO_4]$.[5] Tc_2O_7, generated in situ, or $HTcO_4$ might be the reactive intermediate during the formation of the other known Tc(VII) complexes with the $[TcO_3]^+$ core in the presence of strong, concentrated acids. Namely, complexes of the general formula $[TcO_3Cl(phen)]$ and $[TcO_3Cl(bipy)]$, and some other bidentate aromatic amines, have been prepared along this route but have not been structurally characterized.[6,7] These complexes are insoluble in organic solvents and hydrolyze rapidly back to $[TcO_4]^-$ in the presence of water. Similarly, complexes with the $[TcO_3]^+$ core have been obtained from $[TcO_4]^-$ in the presence of concentrated nitric or sulfuric acid with

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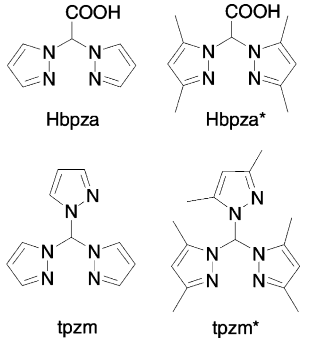
(1) Alberto, R. Technetium. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier Pergamon: Amsterdam, 2003; Vol. 5, p 127.
(2) Abram, U. Rhenium. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier Pergamon: Amsterdam, 2003; Vol. 5, p 271.
(3) Boyd, G. E.; Cobble, J. W.; Nelson, C. M.; Smith, J. W. T. *J. Am. Chem. Soc.* **1952**, *74*, 556.
(4) Herrmann, W. A.; Alberto, R.; Kiprof, P.; Baumgärtner, F. *Angew. Chem., Int. Ed.* **1990**, *29*, 189.
(5) Nugent, W. A. *Inorg. Chem.* **1983**, *22*, 965.
(6) Davison, A.; Jones, A. G.; Abrams, M. J. *Inorg. Chem.* **1981**, *20*, 4300.
(7) Dupreez, J. G. H.; Gerber, T. I. A.; Gibson, M. L. *J. Coord. Chem.* **1990**, *22*, 33.

10.1021/ic701908q CCC: $40.75

Scheme 1



tripods such as $[HB(pz)_3]^-$ or Kläui type ligands.[8−11] It has been speculated that a mixed anhydride of pertechnetic and nitric acid might be an intermediate during the synthesis in concentrated nitric acid. Complexes of Tc(VII) are also accessible via an oxidation pathway from corresponding complexes in the oxidation state +V. This approach recently lead to the preparation and full characterization of the complex $[TcO_3(tacn)]Br$.[12] Only the last method represents an approach to $[TcO_3(L^3)]^+$ complexes which can be transferred, in principle, to a broader variety of ligands L^3.

Due to our interest in novel cores for radiopharmaceuticals, it would be intriguing to explore the $[^{99m}TcO_3]^+$ core for the labeling of targeting molecules. Compared to the $[Tc(CO)_3]^+$ building block, $[TcO_3]^+$ is smaller and expected to affect the binding properties of receptor-targeting biomolecules to a lower extent. To assess such a potential, the synthesis and characterization of corresponding model complexes is fundamental. With routine applications in mind, we seek synthetic pathways to generate $[^{99m}TcO_3]^+$ complexes directly from $[^{99m}TcO_4]^-$ and, if possible, via non-redox pathways. A generalized synthesis of model complexes allows for exploration of their properties, especially redox activities and hydrolytic stabilities, before attempting to make them from water, which represents the ultimate step. We present in here a new approach to Tc(VII) complexes via activation of $[TcO_4]^-$ by the strong Lewis acids benzoyl chloride or $BF_3 \cdot OEt_2$, which form rapidly mixed anhydrides with $[TcO_4]^-$. In these mixed anhydrides, the activated group can be replaced by bi- or tridentate ligands in stoichiometric reactions. The known complexes $[TcO_3Cl(bipy)]$ (**1**) and $[TcO_3Cl(phen)]$ (**2**), as well as the new compounds $[TcO_3(bpza)]$ (**3**), $[TcO_3(bpza^*)]$ (**4**), $[TcO_3(tpzm^*)]^+$ (**6**), and $[ReO_3(tpzm^*)][ReO_4]$ (**7**), have been prepared in this way and have been structurally characterized. The structures of the ligands are depicted in Scheme 1. This synthetic concept can be expanded to further ligands for assessing reactivities and stabilities of the corresponding $[^{99m}TcO_3]^+$ complexes and represents the basis for developing a pure aqueous approach.

Experimental Section

Caution: *^{99}Tc is a weak β^- emitter. All experiments have to be done in laboratories approved for working with low-level radioactive materials.* All reactions were carried out under N_2. Acetone was dried with molecular sieves using standard procedure. $NH_4[TcO_4]$ (Oak Ridge), 2,2′-bipyridine (bipy, Fluka AG, Buchs CH), and 1,10-phenanthroline (phen, Aldrich) were used without further purification. The ligands di-1H-pyrazol-1-ylacetic acid (Hbpza),[13] bis(3,5-dimethyl-1H-pyrazol-1-yl)acetic acid (Hbpza*),[14] 1,1,1-methanetriyltris(1H-pyrazole) (tpzm),[15] and 1,1,1-methanetriyltris(3,5-dimethyl-1H-pyrazole) (tpzm*)[15] were prepared according to literature procedures. Infrared spectra were measured as KBr pellets on Perkin-Elmer BXII. The ^{1}H NMR spectra of $[TcO_3(tpzm^*)]_2[(BF_3)_2O]$ and $[ReO_3(tpzm^*)][ReO_4]$ were recorded on a Varian Mercury 200 MHz spectrometer. The ^{1}H NMR spectrum of $[TcO_3(bpza)]$ and the ^{1}H, ^{19}F, and ^{11}B NMR spectra of $[TcO_3(OBF_3)]^-$ and $[TcO_3(tpzm^*)]_2[(BF_3)_2O]$ were recorded on a Varian Gemini 300 MHz spectrometer. ^{99}Tc NMR spectra were recorded on a Bruker AV2-500. Chemical shifts of ^{99}Tc are referenced relative to the signal of a 0.1 M solution of $(NH_4)[^{99}TcO_4]$ in CD_3OD ($\delta = 0$). ESI$^+$ mass spectra were recorded with a HCT Ultra (Bruker). For analysis of Tc contents in the complexes, single crystals of the respective compounds were weighed with an analytical balance (microgram amounts) and destroyed by stirring in water ($[TcO_3Cl(bipy)]$, $[TcO_3Cl(phen)]$) or DMSO ($[TcO(eg)(bpza^*)]$). The measurements have been carried out by liquid scintillation counting (TRI-CARB 2200CA, Packard, Packard Ultimate Gold XR). HPLC analyses were performed on a Merck Hitachi LaChrom L 7100 pump coupled to an Merck Hitachi LaChrom L7200 tuneable UV detector. Separations were achieved on a Macherey-Nagel C18 reversed-phase column (EC 250/3 Nucleosil 100-5 C18) using a gradient of MeCN/0.1% CF_3COOH as eluent and flow rates of 0.5 mL/min. Method: $t = 0 - 3$ min, 0% MeCN; 3−3.1 min, 0−25% MeCN; 3.1−9 min, 25% MeCN; 9−9.1 min, 25−34% MeCN; 9.1−18 min, 34−100% MeCN; 18−25 min, 100% MeCN; 25−25.1 min, 100−0% MeCN; 25.1−30 min, 0% MeCN.

Syntheses. $[TcO_3Cl(bipy)]$ (1). $(Bu_4N)[TcO_4]$ (40 mg, 0.1 mmol) and bipy (16 mg, 0.1 mmol) were dissolved in benzoyl chloride (5 mL), and the solution was stirred for 30 min at ambient temperature. The product precipitated from the reaction solution as a yellow powder (yield: 23 mg, 69%). Crystals suitable for X-ray diffraction analysis were obtained by layering a benzoyl chloride solution of $(Bu_4N)[TcO_4]$ (1 mL, 0.05 M) with a solution of bipy dissolved in a 1 to 1 mixture of acetonitrile and THF (2 mL, 0.025 M).

Anal. Calcd for $C_{10}H_8N_2O_3ClTc$: Tc, 29.3. Found: Tc, 31.3. IR ($\nu_{Tc=O}$): 904 (vs), 885 (vs), 860 (m) cm^{-1}.

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(8) Pearlstein, R. M. Ph.D. Thesis, 1988.

(9) Joachim, J. E.; Apostolidis, C.; Kanellakopulos, B.; Maier, R.; Ziegler, M. L. *Z. Naturforsch., B* **1993**, *48*, 227.

(10) Banbery, H. J.; Hussain, W.; Evans, I. G.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A.; Schulte, H. J.; Engles, B.; Kläui, W. *Polyhedron* **1990**, *9*, 2549.

(11) Thomas, J. A.; Davison, A. *Inorg. Chem.* **1992**, *31*, 1976.

(12) Braband, H.; Abram, U. *Inorg. Chem.* **2006**, *45*, 6589.

(13) Burzlaff, N.; Hegelmann, I.; Weibert, B. *J. Organomet. Chem.* **2001**, *626*, 16.

(14) Beck, A.; Weibert, B.; Burzlaff, N. *Eur. J. Inorg. Chem.* **2001**, 521.

(15) Reger, D. L.; Grattan, T. C.; Brown, K. J.; Little, C. A.; Lamba, J. J. S.; Rheingold, A. L.; Sommer, R. D. *J. Organomet. Chem.* **2000**, *607*, 120.

[$TcO_3Cl(phen)$] (2). (Bu_4N)[TcO_4] (40 mg, 0.1 mmol) and phen (18 mg, 0.1 mmol) were dissolved in benzoyl chloride (5 mL), and the solution was stirred for 1 h at ambient temperature. The product precipitated from the reaction solution as an orange powder (yield: 24 mg, 65%). Crystals suitable for X-ray diffraction analysis were obtained by layering a benzoyl chloride solution of (Bu_4N)[TcO_4] (1 mL, 0.05 M) with a solution of phen dissolved in a 1 to 1 mixture of acetonitrile and THF (2 mL, 0.025 M). Anal. Calcd for $C_{12}H_8N_2O_3ClTc$: Tc, 27.2. Found: Tc, 26.4. IR ($\nu_{Tc=O}$): 897 (s), 885 (s), 868 (s) cm^{-1}. Due to the complete insolubility of **1** or **2** in any solvent, it was not possible to record NMR spectra.

[$TcO_3(bpza)$] (3). To a solution of Na[TcO_4] (19 mg, 0.1 mmol) in benzoyl chloride (4 mL) was added Hbpza (19 mg, 0.1 mmol) dissolved in 1 mL of acetonitrile, and the new solution was stirred for 1 h at ambient temperature. Dry diethyl ether was added to initiate precipitation, and the yellow precipitant was filtered off (contains product and NaCl). The product was extracted with acetonitrile, which gave yellow green crystals after evaporation of the solvent (yield: 16 mg, 47%). IR: 1673 (vs, $\nu_{as\ C=O}$), 906 (vs, $\nu_{Tc=O}$), 896 (vs, $\nu_{Tc=O}$) cm^{-1}. ^{1}H NMR (CD_3CN): $\delta = 8.32$ (br, 2 H, pz), 8.07 (br, 2 H, pz), 7.06 (br, 1 H, CH), 6.60 ppm (br, 2 H, pz). ^{99}Tc NMR (from reaction solution): $\delta = 220$ ppm ($\Delta\nu_{1/2} = 2500$ Hz).

[$TcO_3(bpza^*)$] (4). (Bu_4N)[TcO_4] (40 mg, 0.1 mmol) was dissolved in benzoyl chloride (3 mL), and then Hbpza* (25 mg, 0.1 mmol) was added with the solution stirred for 1 h at ambient temperature. The product precipitated from the reaction solution as a yellow powder, which was filtered off and dried under vacuum (yield: 35 mg, 90%).

IR ($\nu_{Tc=O}$): 904 (vs), 896 (vs) cm^{-1}. Due to complete insolubility of **4** in any solvent, it was not possible to record NMR spectra.

[$TcO(eg)(bpza^*)$] (5). [$TcO_3(bpza^*)$] **4** (35 mg, 0.09 mmol) was suspended in 5 mL of acetonitrile and stirred at 40 °C for 3 h under ethene. The color of the reaction solution changed rapidly from colorless to blue, and the Tc(V) complex [TcO(eg)(bpza*)] (eg = ethylene glycolato ligand) precipitated immediately. The blue product was filtered off and dried under vacuum (yield: 19 mg, 48%). Anal. Calcd for $C_{14}H_{19}N_4O_5Tc$: Tc, 23.5. Found: Tc, 21.8. IR: 958 (s, $\nu_{Tc=O}$), 653 (m, $\nu_{Tc-O\ glycol}$), 619 (m, $\nu_{Tc-O\ glycol}$) cm $^{-1}$. ^{1}H NMR ($CDCl_3$): $\delta = 2.51$ (s, 6H, CH_3), 2.55 (s, 6H, CH_3), 5.21 (m, 2H, eg), 5.76 (m, 2H, eg), 6.23 ppm (s, 3H, Hpz and CH).

[$TcO_3(tpzm^*)]_2[(BF_3)_2O$] (6). ($Bu_4N$)[$TcO_4$] (40 mg, 0.1 mmol) was dissolved in dry acetone (4 mL), and $BF_3 \cdot OEt_2$ (63 μL, 0.5 mmol) was added. The solution was stirred for 30 min. Then tpzm* (30 mg, 0.1 mmol) dissolved in 1 mL of dry acetone was added. The product precipitated from the reaction solution after the addition of ether as a yellow powder (yield: 35 mg, 67%). IR ($\nu_{Tc=O}$): 905 (vs), 896 (vs) cm^{-1}. ^{1}H NMR (CD_3CN): $\delta = 7.78$ (s, 1H, CH), 6.29 (s, 3H, Hpz), 2.82 (s, 9H, CH_3), 2.54 ppm (s, 9H CH_3). ^{11}B NMR (CD_3CN): $\delta = 2.78$ ppm. ^{99}Tc NMR (CD_3CN): $\delta = 188$ ppm ($\Delta\nu_{1/2} = 5000$ Hz).

[$ReO_3(tpzm^*)$][ReO_4] (7). [Re_2O_7] (60 mg, 0.12 mmol) was dissolved in THF (3 mL), and tpzm* (18 mg, 0.06 mmol) was added. The reaction solution was stirred for 4 h at ambient temperature. The product precipitated from the reaction solution as a colorless powder (yield: 39 mg, 40%). Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into an acetonitrile solution of [ReO_3(tpzm*)][ReO_4].

^{1}H NMR (CD_3CN): $\delta = 7.82$ (s, 1H, CH), 6.34 (s, 3H, Hpz), 2.81 (s, 9H, CH_3), 2.55 ppm (s, 9H CH_3). Anal. Calcd for $C_{16}H_{22}N_6O_7Re_2$: C, 24.55; H, 2.83; N, 10.74. Found: C, 24.92; H, 3.07; N, 10.95. ESI$^+$ MS: $m/z = 533.1$ (M$^+$). To avoid a band overlap of the $\nu_{Re=O}$ stretching of [ReO_4]$^-$ and [ReO_3]$^+$ in the IR spectrum of **7**, [ReO_4]$^-$ was exchanged by [BPh_4]$^-$. [ReO_4]$^-$ was precipitated as TBA[ReO_4] from a water solution of complex **7** (30 mg, 0.04 mmol) by the addition of (TBA)Cl and was filtered off. The addition of $NaBPh_4$ (14 mg, 0.04 mmol) to the aqueous solution yields [ReO_3(tpzm*)][BPh_4] as a colorless solid, which was filtered off and dried under vacuum. IR ($\nu_{Re=O}$): 919, 892 cm^{-1}.

X-ray Diffraction. Crystallographic data were collected at 183(2) K with Mo Kα radiation ($\lambda = 0.7107$ Å) that was monochromated with help of graphite on either a Stoe IPDS diffractometer (**3**) or an Oxford Diffraction Xcalibur system (**1**−**2**, **5**, **7**) with a Ruby detector. Suitable crystals were covered with oil (Infineum V8512, formerly known as Paratone N), mounted on top of a glass fiber, and immediately transferred to the diffractometer. In the case of the IPDS, a maximum of 8000 reflections distributed over the whole limiting sphere were selected by the program SELECT and used for unit cell parameter refinement with the program CELL.[16] Data were corrected for Lorentz and polarization effects as well as for absorption (numerical). In case of the Oxford system, the program suite CrysAlis^{Pro} was used for data collection, semiempirical absorption correction, and data reduction.[17] Structures were solved with direct methods using SIR97[18] and were refined by full-matrix least-squares methods on F^2 with SHELXL-97.[19] The structures were checked for higher symmetry with help of the program Platon.[20] More details on data collection and structure calculation are contained in Table 1 ([ReO_3(tpzm*)][ReO_4], Table S1 (Supporting Information)).

Results and Discussion

Tri- or bidentate ligands do not react directly with [TcO_4]$^-$ to form complexes containing the [TcO_3]$^+$ core. Formally, negatively charged [TcO_4]$^-$ is a 16e$^-$ species with a low tendency to accommodate further ligands or electrons. To render [TcO_4]$^-$ (and other permetalates) more reactive, the

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(16) *STOE-IPDS Software package*; STOE & Cie, GmbH: Darmstadt, Germany, 1999.

(17) *CrysAlis^{Pro} Software system*, vers. 171.32 Oxford; Oxford Diffraction Ltd.: Oxford, U.K., 2007.

(18) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(19) Sheldrick, G. M. *SHELXL97-2: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

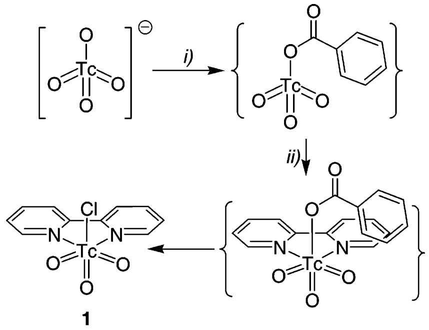
(20) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

Table 1. Crystallographic Data for [TcO_3Cl(bipy)], [TcO_3Cl(phen)], [TcO_3(bpza)], and [TcO(eg)(bpza*)]

param	[TcO_3Cl(bipy)]	[TcO_3Cl(phen)]	[TcO_3(bpza)]	[TcO(eg)(bpza*)]
formula	$C_{10}H_8ClN_2O_3Tc$	$C_{12}H_8ClN_2O_3Tc$	$C_8H_7N_4O_5Tc$	$C_{14}H_{19}N_4O_5Tc$
M_w	337.63	361.65	337.18	421.33
space group	$I2/m$	$I2/m$	$P2_1/n$	$P\bar{1}$
a/Å	7.52742(9)	7.5144(2)	11.741(1)	7.2448(2)
b/Å	11.7377(1)	11.6160(2)	8.1846(8)	8.5727(2)
c/Å	12.8669(1)	13.9303(3)	11.3273(9)	12.7729(3)
α/deg	90	90	90	89.856(2)
β/deg	96.286(1)	97.24(1)	91.12(1)	80.937(2)
γ/deg	90	90	90	84.641(2)
μ/mm^{-1}	1.506	1.419	1.344	0.957
Z	4	4	4	2
V/Å^3	1130.01(2)	1206.25(5)	1088.3(2)	779.90(3)
ρ_{calc}/g cm^{-3}	1.985	1.991	2.058	1.794
R1^{a,c}	0.0236	0.0285	0.0448	0.0205
wR2^{b,c}	0.0680	0.0791	0.1084	0.0503

[a] $R1 = |F_o - F_c|/|F_o|$. [b] $wR2 = [w(F_o^2 - F_c^2)^2/(wF_o^2)]^{1/2}$. [c] $I > 2\sigma(I)$.

Scheme 2. Synthesis of **1**[a]



[a] Key: (i) C_6H_5COCl, rt 1 h; (ii) bipy, rt 30 min.

Lewis acidity of Tc has to be increased. Formation of anhydrides or treatment with strong Lewis acids, such as BF_3, are convenient methods for this purpose. Correspondingly, the reaction of $[TcO_4]^-$ with benzoyl chloride resulted in one new single complex. The ^{99}Tc NMR spectrum of this solution showed a broad signal at 3 ppm ($\Delta\nu_{1/2} = 960$ Hz), a region in which other Tc(VII) complexes have been found. We tentatively assign this signal to an in situ prepared, mixed anhydride complex [TcO_3(OCOPh)] (Scheme 2). Besides the formation of [TcO_3(OCOPh)], one could assume the formation of [TcO_3Cl] as the reactive precursor for further substitution reactions. The chemical shift of [TcO_3Cl] is not known, but the resonance of [TcO_3F] appears at 44 ppm as a very sharp signal ($\Delta\nu_{1/2} = 23$ Hz), according to its high symmetry.[21] Although the shift of [TcO_3Cl] would be different, the line width should be small as well. There was no evidence for such a signal, implying the formation of the mixed anhydride [TcO_3(OCOPh)], due to its higher stability.

This reactive anhydride represents a new, nonvolatile and in situ generated precursor for the synthesis of Tc(VII) complexes with the $[TcO_3]^+$ core. The Tc center in [TcO_3(OCOPh)] is electrophilic, which is mirrored by its moisture sensitivity, resulting in quick hydrolysis to $[TcO_4]^-$ and benzoic acid. Conceptually, the 14e$^-$ species was stabilized by the addition of ligands, giving octahedral 18e$^-$ complexes. Addition of 2 equiv of monodentate ligands, such as pyridine, gave a yellow powder. The IR spectrum revealed a broad band at 893 cm^{-1}, which is different from that for $[TcO_4]^-$ and implies a complex like [TcO_3(OCOPh)(py)$_2$]. However, the reactivity resulted in decomposition at ambient conditions, preventing full characterization.

More stable Tc(VII) complexes could be obtained with bidentate ligands. The addition of 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) to [TcO_3(OCOPh)], prepared in situ, yielded the two prototypic complexes [TcO_3Cl(bipy)] (**1**) and [TcO_3Cl(phen)] (**2**). Complexes **1** and **2** were first synthesized by Davison et al. and characterized by elemental analysis, UV, IR, and Raman spectroscopy, but structural characterization was not possible due to complete insolubility in any solvent.[6] Compound **1** was also synthesized by the reaction of (Bu_4N)[TcO_4] and bipy in benzoyl chloride in 69% yield. [TcO_3Cl(bipy)] is stable as a solid under dry condition, but hydrolysis to $[TcO_4]^-$ was observed in the presence of water. Crystals could be grown from a very slow reaction between two layers: one containing the bipy ligand and the other the [TcO_3(OCOPh)] complex. Presumably, the complex [TcO_3(OCOPh)(bipy)] formed first but remained in solution. Chloride then substituted the benzoate, and crystals grew due to the complete insolubility of **1**. The crystal structure of [TcO_3Cl(bipy)] is shown in Figure 1.

The technetium atom is coordinated to two nitrogens, three facially arranged oxygens and one chlorine in a distorted octahedral environment. The technetium, the oxygen O1, and the chlorine atom are located on a mirror plane of the monoclinic space group $I2/m$. The technetium atom is disordered at two position, above and below the plane formed by the two nitrogen atoms (N1, N1′) and the two carbon atoms (C1, C1′) of the bipy ligand (distances from the plane: Tc1 0.368(1), Tc2 0.424(6) Å). Tc2 has a 2% occupancy.

The Tc1−O2 bond length, 1.703(2) Å, is comparable to those found in [TcO_3(tacn)]$^+$ (1.703(4) Å).[12] The Tc1−O1 bond length (1.714(2) Å) is about 0.01 Å longer due to the trans influence of the chloro ligand. Similar characteristics have been found in the corresponding complex [ReO_3Cl(bipy)].[23] The long Tc−N bond lengths in [TcO_3Cl(bipy)] (2.248(1) Å) reflect the structural trans influence of the oxo

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(21) Casteel, W. J.; Dixon, D. A.; LeBlond, N.; Mercier, H. P. A.; Schrobilgen, G. J. *Inorg. Chem.* **1998**, *37*, 340.

(22) Farrugia, L. J. *ORTEP-3 for Windows-a Version of ORTEP-III with a Graphical User Interface* (*GUI*); University of Glasgow: Glasgow, U.K., 1997.

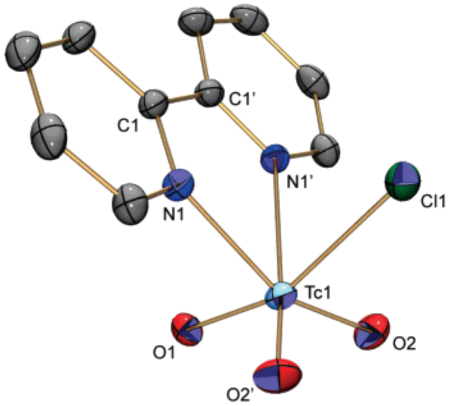

Figure 1. ORTEP representation[22] of the main conformation of [TcO$_3$Cl(bipy)]. Thermal ellipsoids represent 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Tc1−O1 1.714(2), Tc1−O2 1.703(1), Tc1−Cl1 2.532(1), Tc1−N1 2.248(1), O1−Tc1−O2 104.3(1), O2−Tc1−O2′ 107.9(1), Cl1−Tc1−N1 78.7(1), N1−Tc1−N1′ 71.6(1). Symmetry operation: (prime) *x*, −*y*, *z*.

ligands and were also found in [TcO$_3$(tacn)]$^+$ (2.239(4) Å). A very interesting feature for this structure and the ones of the following part is the widening of the O−Tc−O angles to a size similar to a tetrahedral angle. The O−Tc−O bond angles are extended, with 104.3(1) and 107.9(1)° in the same range as in [TcO$_3$(tacn)]$^+$ (106.5(2)°). The opening of the O−Tc−O angles is a typical feature of the *fac*-[TcO$_3$]$^+$ core found in all structures. Since Tc(VII) is formally a d^0 system, ligand field stabilization energies must not be considered. Rather, steric features govern the coordination geometry. Thus, the wide O−Tc−O angles can be understood as a result of minimized steric repulsion by adopting maximized distances between the oxygen atoms.[24]

The IR spectrum of **1** shows the characteristic vibrations for the bipy ligand at 1600−1000 cm^{-1} and the characteristic $\nu_{Tc=O}$ bands at 904, 885, and 860 cm^{-1}.[6]

Compound **2** was synthesized similarly to **1** in 65% yield. Unlike bipy, phen reacted at a slower rate with the mixed anhydride. [TcO$_3$Cl(phen)] is a stable solid under dry conditions but hydrolyzes quickly to [TcO$_4$]$^-$ in the presence of traces of water.

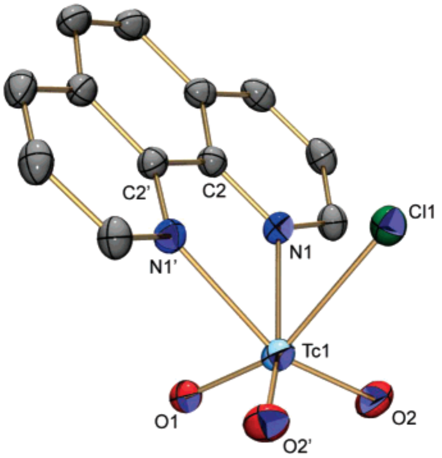

Figure 2. ORTEP representation[22] of the main conformation of [TcO$_3$Cl(phen)]. Thermal ellipsoids represent 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Tc1−O1 1.749(2), Tc1−O2 1.706(1), Tc1−Cl1 2.505(1), Tc1−N1 2.267(1), O1−Tc1−O2 104.3(1), O2−Tc1−O2′ 108.0(1), Cl1−Tc1−N1 77.5(1), N1−Tc1−N1′ 72.0(1). Symmetry operation: (prime) *x*, −*y*, *z*.

The crystal structure of [TcO$_3$Cl(phen)] is shown in Figure 2. The compound crystallizes with lattice constants similar to those of [TcO$_3$Cl(bipy)], and the technetium, the oxygen O1, and the chlorine atoms are again located on a mirror plane of the monoclinic space group *I*2/*m*. As in **1**, the technetium atom in **2** is disordered in two positions above and below the plane formed by the two nitrogen atoms (N1, N1′) and the two carbon atoms (C2, C2′) (distances from the plane (Å): Tc1, 0.334(1); Tc2, 0.285(4)). Tc2 has a 6% occupancy. The O−Tc−O angles are rather similar to those found in **1**. This is reflected in the similar displacements of the technetium atoms from the plane formed by the three oxygen atoms ([TcO$_3$Cl(bipy)], 0.673(1) Å; [TcO$_3$Cl(phen)], 0.677(1) Å). While the Tc−O2 distance of 1.706(1) Å in **2** is in the same range as in **1** (1.703(1) Å), the Tc−O1 bond length (trans position to the chloro ligand) of 1.749(2) Å is significantly longer than in [TcO$_3$Cl(bipy)] (1.714(2) Å). This interesting structural feature correlates to a shorter Tc−Cl distance of 2.505(1) Å, compared to **1** (2.532(1) Å). The difference in the bond length shows the flexibility of the trioxo core with respect to changes in the coordination sphere and reflects the corresponding behavior in the rhenium complex [ReO$_3$Cl(phen)].[25] The Tc−N distances in **2** (2.267(1) Å) are 0.019 Å longer than in **1** implying that bipy is a stronger ligand than phen at least for complexes with the [TcO$_3$]$^+$ core. The IR spectrum of [TcO$_3$Cl(phen)] shows bands at 897, 885, and 868 cm^{-1} which fit very well with the absorptions described by Davison and co-workers for the Tc═O stretch of the complex [TcO$_3$Cl(phen)].[6]

The promising new approach for the synthesis of complexes containing the [TcO$_3$]$^+$ core via the activation of [TcO$_4$]$^-$ by benzoyl chloride was also used for the synthesis of new technetium complexes containing the [TcO$_3$]$^+$ core and the tridentate ligands di-1*H*-pyrazol-1-ylacetate (bpza) and bis(3,5-dimethyl-1*H*-pyrazol-1-yl)acetate (bpza*), respectively. These types of heteroscorpionate ligands are well-known in rhenium chemistry due to their ability to stabilize rhenium in the oxidation states +I,[13,26] +V,[27−29] and +VII.[30] They coordinate in a stereochemically favorable, *fac* geometry.

After activation of Na[TcO$_4$] in benzoyl chloride, and in the presence of Hbpza, [TcO$_3$(bpza)] (**3**) precipitates as a pale yellow-green powder after the addition of ether. The complex is soluble in acetonitrile and THF. This complex is much more stable than **1** or **2**, and no decomposition could

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(23) Sergienko, V. S.; Khodashova, T. S.; Porai-Koshits, M. A. *Koord. Khim.* **1977**, *3*, 1060 (in Russian; *Coord. Chem.*).

(24) Wieghardt, K.; Pomp, C.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 1659.

(25) Lis, T. *Acta Crystallogr.* **1987**, *C43*, 1710.

(26) Peters, L.; Burzlaff, N. *Polyhedron* **2004**, *23*, 245.

(27) Cowley, A. R.; Dilworth, J. R.; Salichou, M. *Dalton Trans.* **2007**, 1621.

(28) Porchia, M.; Papini, G.; Santini, C.; Lobbia, G. G.; Pellei, M.; Tisato, F.; Bandoli, G.; Dolmella, A. *Inorg. Chim. Acta* **2006**, *359*, 2501.

(29) Porchia, M.; Papini, G.; Santini, C.; Lobbia, G. G.; Pellei, M.; Tisato, F.; Bandoli, G.; Dolmella, A. *Inorg. Chem.* **2005**, *44*, 4045.

(30) Burzlaff, N.; Hegelmann, I. *Inorg. Chim. Acta* **2002**, *329*, 147.

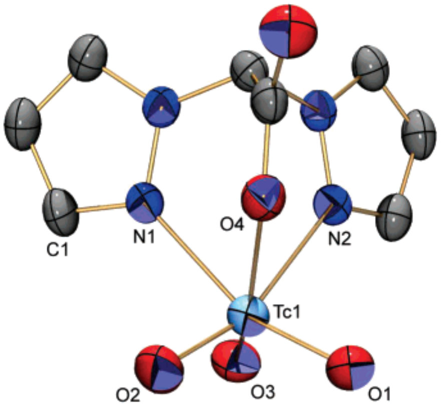

Figure 3. ORTEP representation[22] of [TcO$_3$(bpza)]. Thermal ellipsoids represent 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Tc1−O1 1.690(3), Tc1−O2 1.685(3), Tc1−O3 1.683(3), Tc1−O4 2.155(3), Tc1−N1 2.266(3), Tc1−N2 2.272(3), O1−Tc1−O2 105.8(2), O1−Tc1−O3 104.5(2), O2−Tc1−O3 104.5(2), N1−Tc1−N2 77.1(1), N1−Tc1−O4 75.7(1), N2−Tc1−O4 77.5(1).

be observed over a long period of time under dry conditions. Since the behavior in the presence of water is relevant for later applications, the hydrolytic stability was investigated. Despite the presence of a tridentate ligand and an 18e$^-$ complex, **3** decomposed in a mixture of acetonitrile and water (9:1) within 5 min to [TcO$_4$]$^-$, quantitatively. Thus, **3** is certainly not a candidate for the preparation of the corresponding ^{99m}Tc complexes. Crystals of **3** could be grown, and the structure was elucidated. An ORTEP presentation is given in Figure 3. Complex **3** crystallizes in the centrosymmetric space group $P2_1/n$.

The technetium atom is coordinated in a strongly distorted octahedral geometry. Distortions of the molecular structure are due to restrictions imposed by the tripod ligand and the steric requirements of the terminal oxygen atoms. Accordingly, this results in small N−Tc−N and N−Tc−O4 angles (75.7(1)−77.5(1)°) and expanded O$_{oxo}$−Tc−O$_{oxo}$ angles (104.5(2)−105.8(2)°) approaching again the size of tetrahedral, rather than of octahedral, angles. All Tc−O$_{oxo}$ bond lengths are similar (1.683(3)−1.690(3) Å) and significantly shorter than the shortest Tc−O$_{oxo}$ distance in **1** (1.703(1) Å), **2** (1.706(1) Å), or [TcO$_3$(tacn)]$^+$ (1.703(4) Å).[12] Correspondingly, the Tc−N (2.266(3), 2.272(3) Å) and Tc−O4 (2.155(3) Å) bond lengths are substantially longer, due to the strong trans influence of the oxo ligands. This bond weakening might be responsible for the hydrolytic instability of **3**. The IR spectrum of **3** shows a broad signal at 1673 cm^{-1} for the $\nu_{\text{as C=O}}$ stretching vibration and signals at 906 and 896 cm^{-1} for $\nu_{\text{Tc=O}}$, the expected range for [TcO$_3$]$^+$ complexes with tripod ligands.[9−12]

The ^{1}H NMR spectrum of [TcO$_3$(bpza)] shows one set of broad signals for the bpza ligand, which is significantly shifted to lower field in comparison to the free acetic acid Hbpza.[13] The broad proton peaks are most likely due to an efficient T_2 (spin−spin) relaxation, which is stimulated by scalar couplings to the quadrupolar Tc center (I = 9/2), whereas dynamic exchange, chemical shift anisotropy, or paramagnetic interactions are not the reason for the observed line shape. Since **3** hydrolyzes very quickly, the ^{99}Tc NMR was recorded directly from the reaction solution. The spectrum showed one broad signal (line width 2500 Hz) at 220 ppm, which is in the same range as [TcO$_3$(HB(pz)$_3$)] (196 ppm).[31]

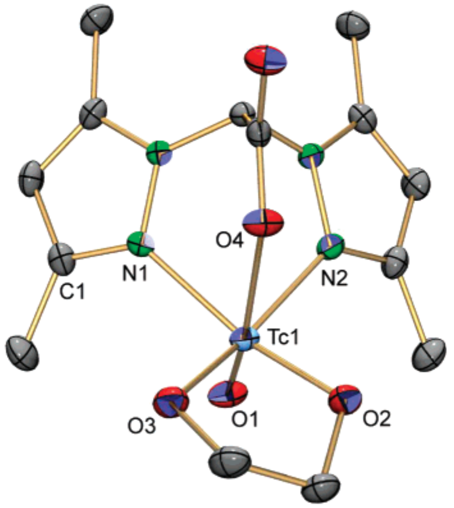

Figure 4. ORTEP representation[22] of [TcO(eg)(bpza*)] (only the major conformation shown). Thermal ellipsoids represent 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Tc1−O1 1.655(1), Tc1−O2 1.916(1), Tc1−O3 1.923(1), Tc1−O4 2.171(1), Tc1−N1 2.141(1), Tc1−N2 2.139(2), O1−Tc1−O2 108.0(1), O1−Tc1−O3 107.1(1), O2−Tc1−O3 83.8(1), N1−Tc1−N2 87.6(1), N1−Tc1−O4 77.7(1), N2−Tc1−O4 77.7(1).

To shield the Tc center from water attack, the more sterically demanding, methylated ligand bpza* was introduced by a similar synthetic approach. The complex [TcO$_3$(bpza*)] (**4**) formed immediately and readily precipitated from the reaction solution as a pale yellow powder without addition of diethyl ether. Complex **4** is stable as a solid but completely insoluble in organic solvents. It was, therefore, not possible to elucidate the structure, and we chose an indirect method for assessing the authenticity of **4**.

Davison and Pearlstein described the [3 + 2] cyclo addition of alkenes to [TcO$_3$]$^+$ complexes which gave the corresponding 1,2-diolato compounds.[32] Thereby, Tc(VII) was reduced to Tc(V). This conversion was used as an indirect proof for the nature of the insoluble complex [TcO$_3$(HB(pz)$_3$)].[31] Accordingly, the reaction of **4**, suspended in acetonitrile, with ethene rapidly gave a blue solution from which the Tc(V) complex [TcO(eg)(bpza*)] (**5**) (eg = ethylene glycolato ligand) precipitated. Compound **5** is stable under ambient conditions in air and in the presence of water and is slightly soluble in CH$_2$Cl$_2$ and CHCl$_3$. The IR spectrum shows a $\nu_{\text{Tc=O}}$ stretching vibration at 958 cm^{-1}, and the bands at 653 and 619 can be assigned to the Tc−O vibrations of the glycol ligand. An X-ray structure analysis confirmed the authenticity of **5** (Figure 4).

[TcO(eg)(bpza*)] crystallized in the triclinic space group $P\bar{1}$. The metal atom is coordinated in a distorted octahedral environment. The ethylene unit of the glycol ligand is disordered, and the two conformations are in a ratio of 57% to 43%. The structure of [TcO(eg)(bpza*)] is very similar to that of the corresponding Tc(V) cation [TcO(eg)(tacn)]$^+$.[12]

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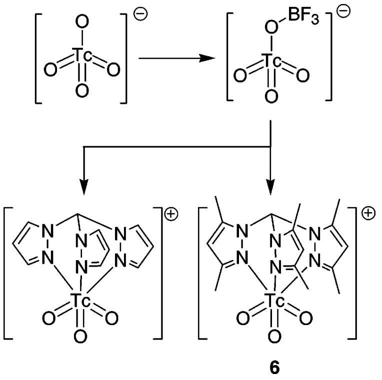
[31] Thomas, J. A.; Davison, A. *Inorg. Chim. Acta* **1991**, *190*, 231.

[32] Pearlstein, R. M.; Davison, A. *Polyhedron* **1988**, *7*, 1981.

Scheme 3. Activation of [$^{99}TcO_4$]$^-$ with $BF_3 \cdot OEt_2$ and Subsequent Reaction with Tripod Ligands



In comparison, the Tc−N, Tc−O_{Oxo}, and Tc−O_{eg} bond lengths in **5** are slightly shorter, and the N−Tc−N and N−Tc−O_4 angles are slightly larger, than in [TcO(eg)(tacn)]$^+$.

The clean and straightforward formation of **5** from **4** suggests that this compound is [TcO_3(bpza*)], although the corresponding X-ray structure or the ^{1}H NMR data could not be obtained.

Activating [TcO_4]$^-$ in benzoyl chloride allowed for the preparation of a series of new Tc(VII) complexes. This synthetic approach can be generalized to other ligands, especially aromatic amines. Since benzoyl chloride is a reactive compound and a strong alkylating reagent, it is a drawback that aliphatic amines cannot be used under these reaction conditions. Furthermore, the release of chloride increases the possibility of reduction product formation. We therefore attempted to use a weaker, but still strong, Lewis acid such as BF_3 for the purpose of [TcO_4]$^-$ activation.

Reaction of [TcO_4]$^-$ and 5 equiv of $BF_3 \cdot OEt_2$ at room temperature in dry acetone or acetonitrile gave a yellow solution. The ^{11}B NMR spectrum of this solution gave one sharp signal at 3.05 ppm, and the ^{19}F NMR, one at 149.80 ppm. These signals are significantly shifted as compared to the signals of $BF_3 \cdot OEt_2$. This implies the formation of a new BF_3 adduct of [TcO_4]$^-$ and rationalizes a mixed anhydride [$TcO_3(OBF_3)$]$^-$. Similar to [TcO_3(OCOPh)], the addition of tridentate ligands to [$TcO_3(OBF_3)$]$^-$ resulted in the formation of *fac*-[TcO_3]$^+$ complexes (Scheme 3).

Tris(pyrazolyl)methane and its derivatives are further attractive tripod ligands. They are of high chemical stability since the C−N bond is stronger than the B−N bond, possess the possibility of introducing further functional groups at the bridge head carbon, and provide, in general, higher complex stability due to their preorganized facial arrangement.[33,34] This class of ligands is, therefore, very interesting for rhenium and technetium with respect to radiopharmaceutical applications. To the best of our knowledge, no corresponding technetium complexes are known. The number of crystallographically characterized rhenium complexes with tpzm or derivatives as tridentate ligands is rather small, and none is known with Re(VII).[27,35−42]

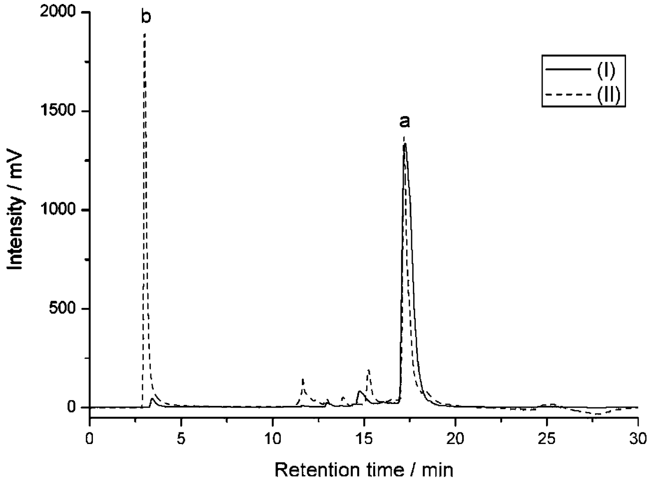


Figure 5. HPLC traces (UV) of [TcO_3(tpzm*)]$_2$[$(BF_3)_2O$] (I) and [ReO_3(tpzm*)][ReO_4] (II): a = [MO_3]$^+$ complex (M = Tc or Re) (17 min); b = [ReO_4]$^-$ (3 min).

Addition of Htpzm or Htpzm* resulted in the formation of the complexes [TcO_3(tpzm)]$^+$ and [TcO_3(tpzm*)]$^+$ (**6**), probably with [$(BF_3)_2O$]$^{2-}$ as a counterion. Both products precipitated from the reaction solution after the addition of ether as yellow powder. Whereas [TcO_3(tpzm)]$_2$[$(BF_3)_2O$] was highly unstable and decomposed immediately under ambient conditions, compound **6** is very stable. Thus, the ^{99}Tc NMR of [TcO_3(tpzm)]$_2$[$(BF_3)_2O$] was recorded directly from the reaction solution. The spectrum showed one broad signal at 209 ppm (line width 1470 Hz), which is in the same range as for compound **3** (220 ppm) and [$TcO_3(HB(pz)_3)$] (196 ppm)[31] and indicates the formation of a Tc(VII) trioxo complex.

Complex **6** is soluble in water. As a confirmation of the higher complex stability of tpzm ligands over bpza, **6** does not hydrolyze up to at least 6 h, in contrast to **1**−**4**, as evident from HPLC analysis. The HPLC trace of **6** (TFA/acetonitrile gradient) showed one single peak with a retention time of 17 min, identical with that of the structurally characterized Re analogue **7** (see later). As shown in Figure 5, the HPLC trace of **7** also shows the counterion [ReO_4]$^-$ with a retention time of about 3 min, which is absent in **6**.

The Tc═O stretching frequencies of **6** appear at 905 and 897 cm^{-1} and are in the same range as for [TcO_3(bpza)] (906, 896 cm^{-1}) and [TcO_3(bpza*)] (904, 896 cm^{-1}).

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(33) Müller, M.; Lork, E.; Mews, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1247.

(34) Wolfgang Kläui, M. B. G. R. H. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 2464.

(35) Middleditch, M.; Anderson, J. C.; Blake, A. J.; Wilson, C. *Inorg. Chem.* **2007**, *46*, 2797.

(36) Herrick, R. S.; Brunker, T. J.; Maus, C.; Crandall, K.; Cetin, A.; Ziegler, C. J. *Chem. Commun.* **2006**, 4330.

(37) Alegria, E. C. B.; Martins, L. M. D. R. S.; Haukka, M.; Pombeiro, A. J. L. *Dalton Trans.* **2006**, 4954.

(38) Alegria, E. C. B.; Martins, L. M. D. R. S.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *J. Organomet. Chem.* **2005**, *690*, 1947.

(39) Reger, D. L.; Brown, K. J.; Smith, M. D. *J. Organomet. Chem.* **2002**, *658*, 50.

(40) Gibson, D. H.; Mashuta, M. S.; He, H. Y. *Acta Crystallogr.* **2001**, *C57*, 1135.

(41) Seymore, S. B.; Brown, S. N. *Inorg. Chem.* **2000**, *39*, 325.

(42) Kunz, P.; Kurz, P.; Spingler, B.; Alberto, R. *Acta Crystallogr.* **2007**, *E63*, M363.

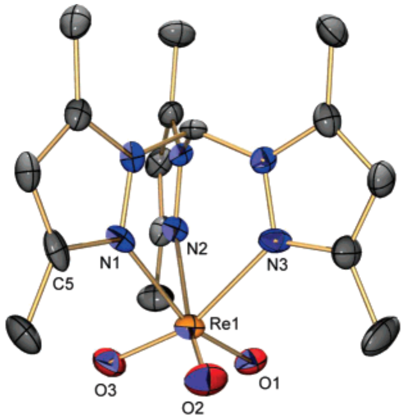

Figure 6. ORTEP representation[22] of the $[ReO_3(tpzm^*)]^+$ cation. Thermal ellipsoids represent 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Re1−O1 1.715(5), Re1−O2 1.715(5), Re1−O3 1.710(5), Re1−N1 2.243(5), Re1−N2 2.229(6), Re1−N3 2.258(5), O1−Re1−O2 104.2(3), O1−Re1−O3 104.6(2), O2−Re1−O3 103.9(2), N1−Re1−N2 76.7(2), N1−Re1−N3 76.0(2), N2−Re1−N3 77.2(2).

The ^1H NMR of the complex showed one set of signals for the tpzm* ligand slightly shifted to higher field as compared to free tpzm*.[15] The signal at 2.78 ppm in the ^{11}B NMR indicated the presence of $[(BF_3)_2O]^{2-}$ as anion. The ^{99}Tc NMR showed one broad signal (line width 5000 Hz) at 188 ppm, which is in the same range as $[TcO_3(bpza)]$ (220 ppm) and $[TcO_3(HB(pz)_3)]$ (196 ppm).[31] This suggests a similar electronic situation at Tc for the complexes **6**, **3**, and $[TcO_3(HB(pz)_3)]$. It is interesting to note that the chemical shifts of the $[TcO_3]^+$ complexes containing the Kläui type ligands (320 ppm)[11] and $[TcO_3(tacn)]^+$ (358 ppm)[12] are shifted to significantly lower fields in comparison to **6**.

The rhenium analogue of **6**, $[ReO_3(tpzm^*)][ReO_4]$ (**7**) was synthesized according to the normal route from $[Re_2O_7]$. To avoid a band overlap of the $\nu_{Re=O}$ stretching of $[ReO_4]^-$ and $[ReO_3]^+$ in the IR spectrum of **7**, $[ReO_4]^-$ was precipitated from a water solution of **7** as TBA$[ReO_4]$ and substituted by $[BPh_4]^-$. The $\nu_{Re=O}$ stretching frequencies of $[ReO_3(tpzm^*)][BPh_4]$ appeared at 919 and 892 cm^{-1}. As its Tc analogue, $[ReO_3(tpzm^*)]^+$ is stable in acetonitrile and water over a long period of time without any hydrolysis. The X-ray crystal structure of the $[ReO_3(tpzm^*)]^+$ cation is shown in Figure 6.

The complex crystallizes in the orthorhombic space group *Pbca*. The Re coordination sphere has a facial arrangement of three oxygens and three nitrogens in a distorted octahedral environment. The Re−O and Re−N bond lengths are very close to the values found in the structurally related complex $[ReO_3(HB(pz)_3)]$.[43] While the O−Re−O angles in $[ReO_3(tpzm^*)][ReO_4]$ (103.9(2)−104.6(2)°) are in the same range as in $[ReO_3(HB(pz)_3)]$ (103.9(1)−104.3(1)°), the N−Re−N angles are slightly smaller in $[ReO_3(tpzm^*)]^+$ (76.0(2)−77.2(2)°) than in $[ReO_3(HB(pz)_3)]$ (77.0(1)−78.2(1)°). In this way the steric repulsion of the methyl groups and the oxygen atoms is minimized, which can be seen in a space-filling model of the $[ReO_3(tpzm^*)]^+$ cation (Figure 7).

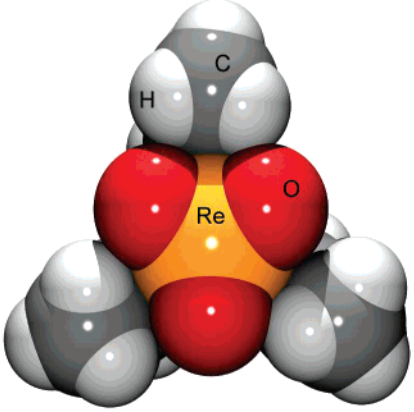

Figure 7. Space-filling model of the $[ReO_3(tpzm^*)]^+$ cation. No steric interaction between the methyl groups and the oxygen atoms can be observed.

This shows the high flexibility of the tpzm* ligand and could be an advantage of this type of ligand for the synthesis of stable $[MO_3]^+$ (M = Tc, Re) complexes containing a well-shielded metal center.

Conclusion

The $[TcO_3]^+$ core is a very interesting motif in the coordination chemistry of technetium, but due to the difficulty in activating the $[TcO_4]^-$, the number of fully characterized compounds is very small. Also, it is difficult to predict which ligand systems can stabilize the $[TcO_3]^+$ core. The two new, reported approaches for the synthesis of rare trioxotechnetium(VII) complexes via the activation of pertechnetate by the strong Lewis acids benzoyl chloride and $BF_3 \cdot OEt_2$ paves the way for the synthesis of new $[TcO_3]^+$ complexes and, thus, could help researchers understand the chemistry and mechanism behind it. Following these new synthetic routes, the two complexes $[TcO_3Cl(bipy)]$ and $[TcO_3Cl(phen)]$ were prepared and structurally characterized. Furthermore, the new activation methods of $[TcO_4]^-$ give three new $[TcO_3]^+$ complexes containing tripodal ligands. The complexes $[TcO_3(bpza)]$, $[TcO_3(bpza^*)]$, $[TcO_3(tpzm^*)]_2[(BF_3)_2O]$, and $[ReO_3(tpzm^*)][ReO_4]$ were synthesized and fully characterized. From a radiopharmaceutical point of view, $[TcO_3(tpzm^*)]_2[(BF_3)_2O]$ has especially interesting reactivity and promising properties (water solubility and stability) for further studies. Corresponding studies with ^{99}Tc and ^{99m}Tc are currently being undertaken in our laboratories.

Acknowledgment. We acknowledge financial support from Mallinckrodt Med. BV, Petten, The Netherlands, and from the University of Zürich (Y.T.)

Supporting Information Available: Details on the data collection and structure calculation of **7** and X-ray crystallographic data in CIF format for all X-ray structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(43) Degnan, I. A.; Herrmann, W. A.; Herdtweck, E. *Chem. Ber.* **1990**, *123*, 1347.