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Synthesis, Characterization, and Structures of R_3EOTcO_3 Complexes ($E = C$, Si, Ge, Sn, Pb) and Related Compounds

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$AgTcO_4$ reacts with R_3ECl compounds (E = C, Si, Ge, Sn, Pb; R = Me, ^{i}Pr, ^{t}Bu, Ph), $^tBu_2SnCl_2$, or PhMgCl under formation of novel trioxotechnetium(VII) derivatives. The carbon and silicon derivatives readily undergo decomposition, which was proven by ^{99}Tc NMR spectroscopy and the isolation of decomposition products such as $[TcOCl_3(THF)(OH_2)]$. Compounds $[Ph_3GeOTcO_3]$, $[(THF)Ph_3SnOTcO_3]$, $[(O_3TcO)Sn^tBu_2(OH)]_2$, and $[(THF)_4Mg(OTcO_3)_2]$ are more stable and were isolated in crystalline form and characterized by X-ray diffraction.

Introduction

Coordination and organometallic compounds of technetium(VII) are still relatively rare, especially with respect to the well-known rhenium(VII) chemistry.[1−4] This is mainly due to the differences in the redox potentials of TcO_4^- and ReO_4^- ($TcO_4^-/TcO_2 = +0.747$ V vs $ReO_4^-/ReO_2 = +0.510$ V),[5] and the lack of suitable technetium(VII) precursors. The facile reduction of technetium(VII) limits the number of compounds that are accessible for this oxidation state, and the volatility of most of the readily accessible technetium(VII) compounds restricts their use in routine procedures with respect to the radioactivity of technetium. Unlike Re_2O_7, which possesses a polymeric structure consisting of tetrameric subunits with preformed tetrahedral and octahedral units (Figure 1),[6] Tc_2O_7 is a centrosymmetric molecule with Tc−O distances of 1.68 Å (terminal) and 1.84 Å (bridging).[7] Thus, some of the reactivities of the oxides can be explained by their structures, particularly the formation of the trioxorhenim(VII) core can be predicted by means of the preformed $\{ReO_3\}$ building blocks in Re_2O_7. Such reactivity is not observed for the molecular technetium oxide, and other precursors are required.

The synthesis of $\{TcO_3\}^+$ complexes from pertechnetate with chelating ligands in the presence of strong acids is restricted to a comparatively small number of (preferably tripodal) chelators and technetium fluorides.[8,9] It is assumed that the initially formed pertechnetic acid, $HTcO_4$, or mixed anhydrides formed from $HTcO_4$ and strong acids serve as the real precursors in such reactions. The synthesis of $MeTcO_3$ and some related products from Me_4Sn and Tc_2O_7 is one of the rare examples in which the oxide is used as a precursor.[10]

Some stable trioxotechnetium(VII) compounds have been prepared by the oxidation of technetium(V) compounds containing powerful chelators. Derivatives of $[^{99}TcO_3(tacn)]Br$ (tacn = 1,4,7-triazacyclononane) are particularly remarkable[11] because their ^{99m}Tc analogues may serve as a new approach to technetium-labeled bioconjugates for nuclear-medical imaging.[11b,12]

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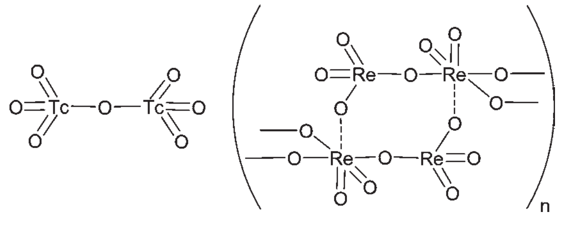

Figure 1. Structures of Tc_2O_7 and Re_2O_7.

Another apparently suitable precursor for trioxotechnetium(VII) compounds, $Me_3SiOTcO_3$, is described in an early report of Nugent,[13] and its reactivity has been proven for the synthesis of a number of arylimidotechnetium(VII) compounds[14] but has not yet found more attention for ongoing reactions. This is readily understood by the reported sensitivity of this compound, which is much higher than that of its rhenium analogue. $Me_3SiOReO_3$ serves as important precursor for rhenium(VI) alkoxides and organometallic rhenium oxides such as $Re_2O_3Me_6$, $Re_2O_4(CH_2CMe_3)_4$, or $R'ReO_3$ (R' = aryl),[15] and also the heavier congoners $R_3GeOReO_3$ and $R_3SnOReO_3$ (R = alky, aryl) have been known for a long time.[16]

Presently, we are searching for suitable precursors for convenient access to technetium(VII) complexes. As part of this work, we report in the present paper about the syntheses and properties of R_3EOTcO_3 complexes (E = C, Si, Ge, Sn, Pb; R = alkyl, aryl) and related compounds.

Results and Discussion

Reactions of $AgTcO_4$ with 1 equiv each of Ph_3CCl or R_3SiCl (R = Me, ^{i}Pr, Ph, $Me_2{}^t$Bu) in dry tetrahydrofuran (THF), $(Me_3Si)_2O$, benzene, or acetonitrile result in the formation of Ph_3COTcO_3 or $R_3SiOTcO_3$. During the reactions, the sparingly soluble, yellow $AgTcO_4$ slowly dissolves and colorless AgCl is precipitated. The reactions can readily be tracked by ^{99}Tc NMR. After about 15 min, the narrow pertechnetate peak at $\delta = 18.52$ ppm (chemical shift in THF, $\Delta\nu_{1/2} = 30$ Hz; reference value $\delta = 0$ ppm in H_2O) disappears and new singlets with larger half-line widths appear in the same region of the spectra (cf. Table 1 and Figure 2). This area is characteristic for tetrahedral technetium(VII) complexes, and also the signal of TcO_3F is detected there.[9,11b] Compared to pertechnetate, all novel technetium(VII) complexes show signals with larger line widths, which is in agreement with the significant electrical quadrupole moment of ^{99}Tc ($Q = -0.19(5) \times 10^{-28}$ m^2), which broadens the signals of compounds with low molecular symmetry.[1,4]

Table 1. ^{99}Tc NMR Data of R_3EOTcO_3 and Related Compounds

compound/solvent	$\delta(^{99}Tc)$ in ppm[a]	$\Delta\nu_{1/2}$ in Hz	ref
$Me_3SiOTcO_3$/toluene	−0.07	not reported	13
$Me_3SiOTcO_3/(Me_3Si)_2O$	11.24	75	
Ph_3COTcO_3/THF	67.27	1045	
$Ph(O)COTcO_3$/PhCOCl	3.00	960	11b
$FTcO_3$/HF	44	23	9a
$^i Pr_3SiOTcO_3$/THF	8.78	127	
$^t BuMe_2SiOTcO_3$ /THF	42.70	307	
$Ph_3SiOTcO_3$/THF	68.30	1572	
$Ph_3GeOTcO_3$/THF	25.15	374	
$Ph_3PbOTcO_3$/THF	6.97	102	
$(THF)Ph_3SnOTcO_3$/THF	−5.10	237	
$[(OH)^t Bu_2SnOTcO_3]_2$/THF	−2.46	293	
$Me_3SnOTcO_3$/THF	−1.2	not reported	10
$(THF)_4Mg(OTcO_3)_2$/THF	−38	120	

[a] With respect to TcO_4^- in H_2O.

We were not able to isolate the R_3EOTcO_3 (E = C, Si) compounds from the reaction solution in crystalline form. The products are oils or jellylike compounds after removal of the solvents. They solidify at temperatures < −10 °C and undergo a rapid decomposition under the influence of moisture, as can be seen by a prolonged darkening (from pale yellow to dark brown) upon storage of the reaction mixtures even under inert conditions. This is most probably due to the reduction of technetium. The rate of decomposition of the technetium(VII) compound depends on the solvents used (THF > acetonitrile > $(Me_3Si)_2O \approx$ benzene) and can be readily tracked by the decreasing intensity of the ^{99}Tc NMR signal.

In two cases, we were able to isolate the decomposition products of such reaction mixtures: (i) colorless crystals of $(Ph_3Si)_2O$ were isolated from the reaction of $AgTcO_4$ with 1 equiv of Ph_3SiCl in dry THF, and (ii) yellow crystals of $[TcOCl_3(OH_2)(THF)]$ appeared when $^i Pr_3SiOTcO_3$ in $^i Pr_3SiCl$ was stored over a period of several weeks. The formation of the first product can be understood by the assumption of an equilibrium between $Ph_3SiOTcO_3$ and $(Ph_3Si)_2O/Tc_2O_7$, as was also observed for analogous rhenium compounds,[17] while isolation of the technetium(V) oxychloride is direct proof of the reductive and hydrolytic degradation of the primary reaction product $^i Pr_3SiOTcO_3$. The formation of trichlorooxotechnetium(V) from $^i Pr_3SiOTcO_3$ with an excess of $^i Pr_3SiCl$ is reproducible; for crystallization of its THF/H_2O adduct, however, a well-balanced ratio between these ligands is required. This is best achieved when carefully dried solvents and glassware and a standard Schlenk technique are used. The small amount of water that is required for hydrolysis/complexation is then released from the glass walls and migrates into the reaction mixture during the manipulations, keeping in mind that the reactions are done at the 0.1 mmol scale.

$[TcOCl_3(OH_2)(THF)]$ is a solvent adduct of one of the three known neutral technetium oxychlorides: TcO_3Cl, $TcOCl_4$, and $TcOCl_3$. None of these compounds has been isolated in crystalline form so far. Previous reports describe $TcOCl_3$ as a product of the photochemical decomposition of $TcOCl_4$. It can also be synthesized directly by chlorination of TcO_2 at 300−350 °C. The IR spectrum of $TcOCl_3$ shows a strong band at 1017 cm^{-1}, which can be assigned to the Tc=O vibration. The compound is sensitive to hydrolysis and disproportionates with water to TcO_2 and $HTcO_4$.[17] Yellow single crystals of $[TcOCl_3(OH_2)(THF)]\cdot 2THF$ were obtained by removal of the solvent from the reaction mixture and recrystallization of the resulting reddish oil from a THF/acetonitrile mixture under inert conditions. The crystals are

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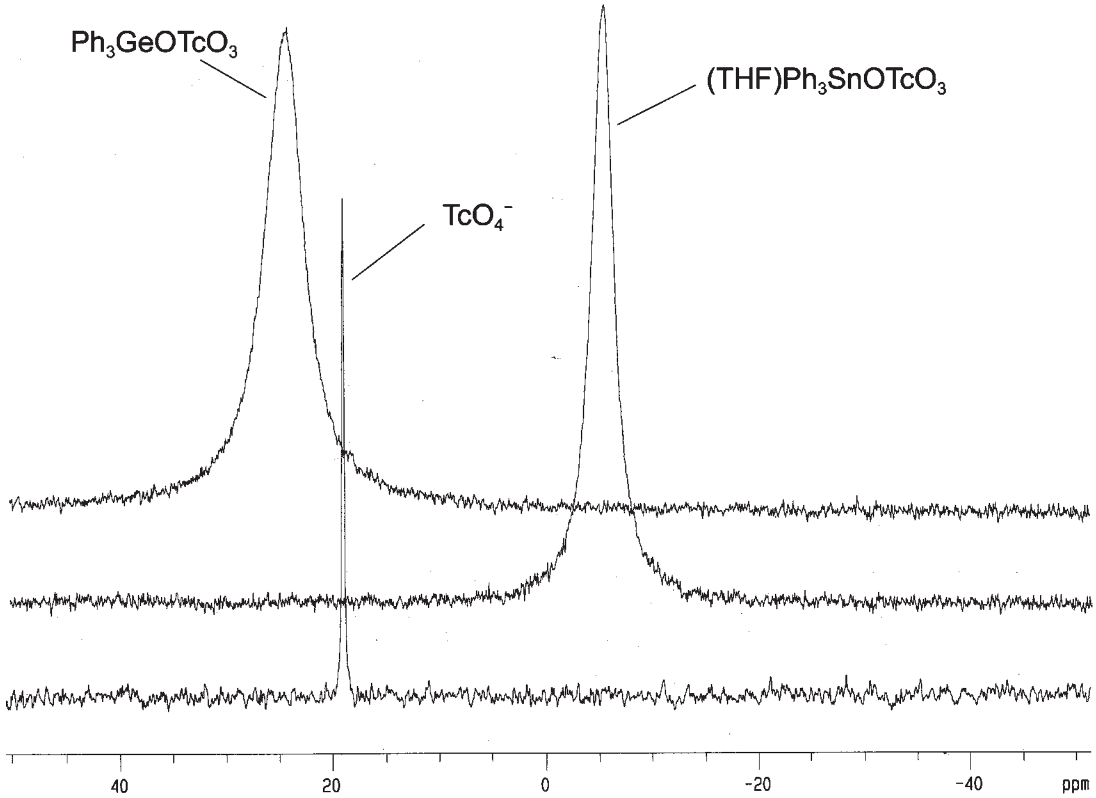

Figure 2. ^{99}Tc NMR spectra of TcO_4^-, $Ph_3GeOTcO_3$, and $(THF)Ph_3SnOTcO_3$. A full collection of the spectra is deposited as Supporting Information.

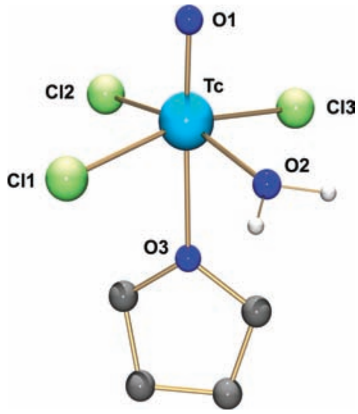

Figure 3. Molecular structure of $[TcOCl_3(OH_2)(THF)]$. THF hydrogen atoms are omitted for clarity.

very sensitive and rapidly decompose upon contact with air or moisture.

Figure 3 illustrates the molecular structure of $[TcOCl_3(OH_2)(THF)]$. Selected bond lengths and angles of the complex are given in Table 2. The technetium atom is coordinated in a distorted octahedral environment, with the oxo ligand and coordinated THF molecule in the trans position to each other. The technetium atom is situated about 0.249 Å above the plane, which is formed from the aqua and three chloro ligands, toward the oxo ligand. The Tc−O3 bond is slightly longer than the Tc−O bonds in $[TcCl_4(THF)_2]$ (Tc−O = 2.112 Å), so far the only other structurally characterized technetium−tetrahydrofuran complex.[18] This can be understood by the trans influence of the oxo ligand in $[TcOCl_3(OH_2)(THF)]$. The positions of the hydrogen atoms of the aqua ligand were derived from peaks of the electron density in the final Fourier map. Both hydrogen atoms are involved in hydrogen bonds to two solvent THF molecules in the unit cell of the structure.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in $[TcOCl_3(OH_2)(THF)]$

Tc−O1	1.620(3)	Tc−Cl1	2.337(1)
Tc−O2	2.037(3)	Tc−Cl2	2.316(1)
Tc−O3	2.290(3)	Tc−Cl3	2343(1)
O1−Tc−O3	175.4(2)	O1−Tc−Cl1	97.9(2)
O1−Tc−O2	96.8(2)	Cl1−Tc−Cl2	89.49(6)

Because isolation of the $R_3SiOTcO_3$ and R_3COTcO_3 compounds in crystalline form was not successful, reactions with the higher homologues germanium, tin, and lead were carried out. The treatment of $AgTcO_4$ with an equivalent amount of Ph_3GeCl in dry THF at room temperature affords, after removal of AgCl and reduction of the volume of the solvent, colorless crystals of the composition $Ph_3GeOTcO_3$. The ^{99m}Tc NMR spectrum exhibits a signal at 25.2 ppm, which indicates the formation of a tetrahedral technetium(VII) compound. The IR spectrum reveals an intense band at 895 cm^{-1} belonging to the Tc=O vibration. A broad band in the region of 800−850 cm^{-1} can be assigned to the vibrations of the Tc−O−Ge bridge. Figure 4a illustrates the molecular structure of $Ph_3GeOTcO_3$. Selected bond lengths and angles for the complex are presented in Table 3. The terminal Tc=O bonds (1.669−1.679 Å) are within the expected range for Tc−O double bonds. The Tc−O bond to the bridging oxygen atom is with 1.785(4) Å slightly longer. The Tc−O−Ge bridge exhibits an angle of 142.4(3)°.

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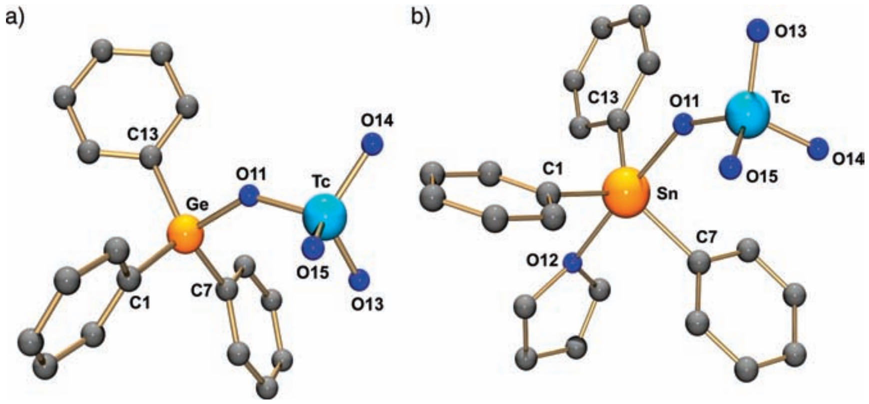

Figure 4. Molecular structures of (a) $Ph_3GeOTcO_3$ and (b) $[(THF)Ph_3SnOTcO_3]$. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in $Ph_3GeOTcO_3$ and $[(THF)Ph_3SnOTcO_3]$

	$Ph_3GeOTcO_3$	$[(THF)Ph_3SnOTcO_3]$
Ge/Sn−O11	1.853(4)	2.211(4)
Ge/Sn−C1	1.905(7)	2.132(5)
Ge/Sn−C7	1.931(7)	2.119(5)
Ge/Sn−C13	1.923(8)	2.119(5)
Sn−O12		2.327(3)
Tc−O11	1.785(4)	1.738(4)
Tc−O13	1.677(5)	1.689(7)
Tc−O14	1.679(5)	1.684(6)
Tc−O15	1.669(5)	1.594(7)
Tc−O11−Ge/Sn	142.4(3)	147.3(2)
O11−Tc−O13	108.8(2)	108.7(3)
O11−Tc−O14	109.5(3)	110.8(2)
O11−Tc−O15	110.0(3)	110.6(3)
C1−Ge/Sn−O11	103.9(2)	91.7(2)
C1−Ge/Sn−C7	116.4(3)	122.5(2)
C7−Ge/Sn−C13	116.2(3)	123.3(2)
O11−Sn−O12		177.1(1)

Analogous $Ph_3SiOReO_3$ and $Ph_3GeOReO_3$ compounds are described but not structurally characterized.[19] A comparison of $Ph_3GeOTcO_3$ with the structurally studied $Me_3SiOReO_3$ shows a number of similarities. The rhenium atom has a tetrahedral coordination environment, with the Re═O bonds (1.55−1.72 Å) being in the range of typical Re═O double bonds. The Si−O−Re angle of 164° is somewhat larger than the Ge−O−Tc angle in $Ph_3GeOTcO_3$. Moreover, the bond between the rhenium atom and the bridging oxygen atom (1.67(8) Å) is slightly shorter than the bridging Tc−O bond in $Ph_3GeOTcO_3$.[20]

The analogous reaction of $AgTcO_4$ and 1 equiv of Ph_3SnCl in dry THF resulted in the formation of the related tin compound $[(THF)Ph_3SnOTcO_3]$, which contains one additional coordinated THF molecule. In contrast to the reactions of the carbon, silicon, or germanium compounds, no rapid darkening of the reaction solution was observed. Merely, a slight yellow color was detected after standing for several days. $[(THF)Ph_3SnOTcO_3]$ can be isolated as colorless crystals directly from the reaction mixture. The compound is stable in air but moisture-sensitive. The ^{99}Tc NMR spectrum exhibits a signal at −5.1 ppm. The addition of water results in a decrease of this signal and the appearance of the narrow $HTcO_4/TcO_4^-$ signal at 18 ppm. The ^{119}Sn NMR spectrum shows a broad signal (line width 241 Hz) at −110.138 ppm. There is no evidence of couplings between technetium and tin. The IR spectrum reveals an intense band at 887 cm^{-1}, which can be assigned to the Tc═O vibration. A broad band in the region at 845 cm^{-1} can be assigned to the vibration of the Tc−O−Sn bridge.

Figure 4b depicts the molecular structure of $[(THF)Ph_3SnOTcO_3]$. Bond lengths and angles are compared to the corresponding values of $Ph_3GeOTcO_3$ in Table 3. The bonding situation in the tin compound is similar to that in $Ph_3GeOTcO_3$. The terminal Tc═O bonds (1.594−1.689 Å) are within the same range, and the bridging Tc−O bond of 1.738(4) Å is slightly shorter than the corresponding bond in the germanium compound. The tin atom is coordinated in a trigonal-bipyramidal environment. The bridging oxo ligand and the oxygen atom of the THF molecule occupy the axial positions, while the three phenyl residues are arranged equatorially.

The corresponding lead compound $Ph_3PbOTcO_3$ can be synthesized by the treatment of $AgTcO_4$ with an equivalent amount of Ph_3PbCl in dry THF. The compound was isolated from the reaction mixture as a colorless powder and characterized by ^{99}Tc NMR and IR spectroscopy. The ^{99}Tc NMR spectrum exhibits a signal at 6.79 ppm. The IR spectrum reveals, as for $Ph_3GeOTcO_3$ and $(THF)Ph_3SnOTcO_3$, an intense band at 891 cm^{-1} belonging to the Tc═O vibration and a broad band in the region at 856 cm^{-1}, which can be assigned to the vibrations of the Tc−O−Pb bridge.

We were not able to isolate a crystalline tin compound with two pertechnetate units during reactions of $^tBu_2SnCl_2$ with 2 equiv of $AgTcO_4$, but its first hydrolysis product was the tetranuclear $[(O_3TcO)Sn^tBu_2(OH)]_2$. The ^{99}Tc NMR spectra of the reaction mixture of the isolated and redissolved complex show only one signal at −2.46 ppm with a line width of 293 Hz. This indicates that hydrolysis proceeds rapid, mainly because of traces of moisture in the tin compound used. No ^{119}Sn NMR signal was observed, which may be explained by a rapid equilibrium between the hydroxo-bridged dimer of Figure 5 and the related monomers in solution. The monomers are already preformed in the solid-state structure, which is evident by two short [2.058(8) Å] and two long [2.177(8) Å] Sn−O bonds. Such a bonding pattern and spectroscopic behavior is frequently observed for

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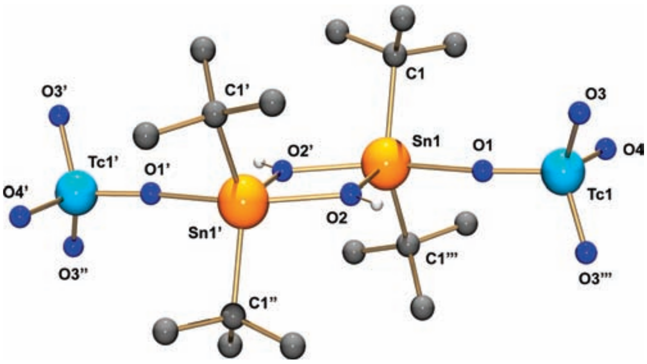

Figure 5. Molecular structure of $[(O_3TcO)Sn^tBu_2(OH)]_2$. Hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in $[(O_3TcO)Sn^tBu_2(OH)]_2$

Sn1−O1	2.24(1)	Tc1−O1	1.67(1)
Sn1−C1	2.187(9)	Tc1−O3	1.651(9)
Sn1−O2	2.058(8)	Tc1−O4	1.68(1)
Sn1−O2′	2.177(8)		
Sn1−O1−Tc1	167.9(7)	O1−Sn1−O2	82.6(4)
O1−Tc1−O3	109.5(4)	O1−Sn1−C1	92.8(3)
Sn1−O2−Sn1′	109.5(4)		

diorganodistannoxanes and is also found for the parent tin halides $[^tBu_2SnX(OH)]_2$ (X = F, Cl, Br).[21]

Colorless crystals of the composition $[(O_3TcO)Sn^tBu_2(OH)]_2 \cdot 2THF$ were obtained directly from the reaction mixture. Figure 5 depicts the molecular structure of the compound. Bond lengths and angles are summarized in Table 4. $[(O_3TcO)Sn^tBu_2(OH)]_2$ contains two pentacoordinate tin atoms, which are connected by two OH bridges. The asymmetric unit contains only one-fourth of the dimeric molecule, while the rest of the molecule is generated by inversion and mirror symmetry. Consequently, the central Sn_2O_2 ring is planar, and the atoms O1 and Tc1 are found in the same plane. The hydrogen atoms of the OH bridges are both involved in hydrogen bonds to the two cocrystallized THF molecules.

The terminal Tc═O bonds (1.65−1.68 Å) are within the expected range for Tc−O double bonds. Unlike the situation in $Ph_3GeOTcO_3$ and $[(THF)Ph_3SnOTcO_3]$, the Tc−O bond to the bridging oxygen atom O1 is with 1.67(1) Å in the same range.

The reaction of $AgTcO_4$ with 2 equiv of PhMgCl in THF resulted in the formation of $[(THF)_4Mg(OTcO_3)_2]$. It is most likely that the first reaction product, $PhMg(OTcO_3)$, in solution rapidly is involved in the Schlenk equilibrium of Grignard reagents with PhMgPh and $(O_3TcO)Mg(OTcO_3)$. Stabilization of the latter compound by the formation of the THF adduct might be one of the reasons that this equilibrium is almost quantitatively shifted to the side of $[(THF)_4Mg(OTcO_3)_2]$, as is also indicated by the appearance of only one ^{99}Tc NMR signal at −38 ppm.

$[(THF)_4Mg(OTcO_3)_2]$ is air- and moisture-sensitive and rapidly decomposes at room temperature. It crystallizes as colorless polyhedra. Figure 6 illustrates the molecular structure of the compound. Selected bond lengths and angles are summarized in Table 5. The magnesium atom is coordinated in a distorted octahedral environment with the two pertechnetate units in the trans position to each other. The coordination environments of the two technetium atoms are almost perfectly tetrahedral. The terminal Tc═O bonds (1.65−1.69 Å) are within the expected range for Tc−O double bonds. The Tc−O1 bond of 1.706(9) Å is only slightly longer.

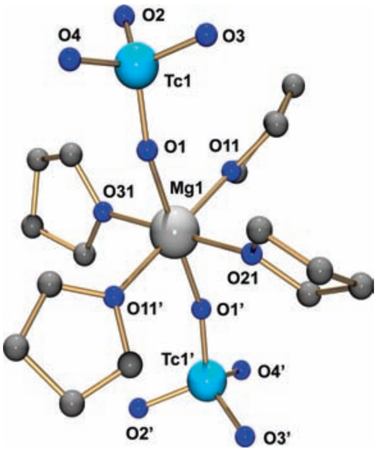

Figure 6. Molecular structure of $[(THF)_4Mg(OTcO_3)_2]$. Hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) in $[(THF)_4Mg(OTcO_3)_2]$

Tc1−O1	1.706(9)	Mg−O1	2.050(9)
Tc1−O2	1.69(1)	Mg−O11	2.074(9)
Tc1−O3	1.67(2)	Mg−O21	2.11(2)
Tc1−O4	1.65(1)	Mg−O31	2.11(2)
O1−Mg−O1′	178.8(9)	Mg−O1−Tc1	163.0(6)
O1−Mg−O11	90.7(4)	O1−Tc1−O2	110.6(6)
O11−Mg−O21	90.5(4)	O2−Tc1−O3	109.8(7)

In summary, it can be stated that mixed anhydrides of pertechnetic acid are readily accessible by the reactions of $AgTcO_4$ with compounds of the composition R_3ECl (E = C, Si, Ge, Sn, Pb), R_2SnCl_2, or RMgCl. ^{99}Tc NMR is a valuable tool to study their formation and decomposition in solution. Particularly, the carbon and silicon compounds are of moderate stability and slowly decompose in the reaction mixture under reduction of the metal. The corresponding germanium, tin, and lead compounds are of higher stability and can be isolated in crystalline form. They may possess potential as precursors for the synthesis of further technetium(VII) compounds.

Experimental Section

Materials. All reagents were reagent-grade and were used without further purification. Reactions were performed using a standard Schlenk technique. Solvents were analytical-grade and were flushed with argon and carefully dried prior to use. $AgTcO_4$ was prepared from $(NH_4)TcO_4$ and $AgNO_3$ following a standard procedure.[22]

Physical Measurements. IR spectra were measured as KBr pellets on a Shimadzu FTIR spectrometer between 400 and 4000 cm^{-1}. Technetium elemental analyses were done by liquid scintillation measurements. NMR spectra were taken with a JEOL 400 MHz multinuclear spectrometer.

Radiation Precautions. ^{99}Tc is a weak β^- emitter (E_{max} = 0.292 MeV) with a half-life of 2.12 × 10^5. Normal glassware provides adequate protection against the weak β radiation when milligram amounts are used. Secondary X-rays (bremsstrahlung), however,

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[21] (a) Davies, A. G. Diorganotin Oxides and Hydroxides. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Oxford, U.K., 2007; Vol. *3*, p 847. (b) Chandrasekhar, V.; Singh, P.; Gopal, K. *Appl. Organomet. Chem.* **2007**, *21*, 483. (c) Puff, H.; Hevendehl, H.; Höfer, K.; Reuter, H.; Schuh, W. *J. Organomet. Chem.* **1985**, *287*, 163.

[22] Keller, C.; Kanellakopulos, B. *Radiochim. Acta* **1963**, *1*, 107.

Table 6. X-ray Structure Data Collection and Refinement Parameters

	$[TcOCl_3(OH_2)(THF)]\cdot 2\ THF$	$Ph_3GeOTcO_3$	$([THF)Ph_3SnOTcO_3]$	$[(O_3TcO)^tBu_2Sn(OH)]_2\cdot 2\ THF$	$[(THF)_4Mg(OTcO_3)_2]$
formula	$C_{12}H_{26}Cl_3O_5Tc$	$C_{18}H_{15}GeO_4Tc$	$C_{22}H_{23}O_5SnTc$	$C_{24}H_{54}O_{12}Sn_2Tc_2$	$C_{16}H_{32}MgO_{12}Tc_2$
M_w	454.68	465.89	584.09	968.05	636.73
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic
a/Å	8.294(1)	9.478(1)	18.720(1)	16.406(5)	10.322(5)
b/Å	10.725(1)	38.683(4)	14.476(1)	13.122(5)	16.50(2)
c/Å	11.911(1)	9.899(1)	16.780(1)	9.959(5)	14.416(7)
α/deg	104.19(1)	90	90	90	90
β/deg	109.40(1)	101.68(1)	102.89(1)	121.29(1)	90
γ/deg	97.40(1)	90	90	90	90
V/Å^3	942.9(2)	3554.2(6)	4432.6(4)	1832.1(1)	2455(3)
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$C2/m$	$Pbcn$
Z	2	8	8	2	4
D_{calcd}/g cm^{-3}	1.602	1.741	1.750	1.755	1.723
μ/mm^{-1}	1.203	2.486	1.779	2.135	1.205
no. of reflns	10 059	17 510	25 944	4903	8703
no. of indep reflns	5036	7385	11 847	1730	2164
no. of param	190	433	523	100	152
R1/wR2	0.0502/0.1226	0.0499/0.0916	0.0470/0.1120	0.0577/0.0897	0.0660/0.1361
GOF	0.967	0.848	0.900	0.937	0.746

play a role when larger amounts of ^{99}Tc are handled. All manipulations were done in a laboratory approved for the handling of radioactive materials. Particular care was taken during the manipulation of volatile materials to avoid any contamination.

Syntheses of $[R_3EOTcO_3]$ (E = C, Si, Ge, Sn, Pb; R_3 = Me, ^{i}Pr, ^{t}Bu, Ph). $AgTcO_4$ (0.1 mmol) was suspended in 3 mL of dry THF, $(Me_3Si)_2O$, benzene, or MeCN, and the corresponding R_3ECl (0.1 mmol) was added. The mixture was stirred at room temperature for 2 h, and the precipitated AgCl was removed by filtration. In the case of Ph_3GeCl, Ph_3SnCl, and Ph_3PbCl, the solution was reduced under vacuum to 0.5 mL and stored at −20 °C for 1 day. $Ph_3GeOTcO_3$ and $(THF)Ph_3SnOTcO_3$ were deposited as colorless crystals from THF solutions and $Ph_3PbOTcO_3$ as a colorless powder.

Data for Ph_3COTcO_3. ^{99}Tc NMR (THF): δ 67.3 ppm. $\Delta\nu_{1/2}$ = 1045 Hz.

Data for $Me_3SiOTcO_3$. ^{99}Tc NMR $[(Me_3Si)_2O]$: δ 11.2 ppm. $\Delta\nu_{1/2}$ = 75 Hz.

Data for $^iPr_3SiOTcO_3$. ^{99}Tc NMR (THF): δ 8.8 ppm. $\Delta\nu_{1/2}$ = 127 Hz.

Data for $Ph_3SiOTcO_3$. ^{99}Tc NMR (THF): δ 68.3 ppm. $\Delta\nu_{1/2}$ = 1572 Hz.

Data for $Me_2{}^tBuSiOTcO_3$. ^{99}Tc NMR (THF): δ 42.7 ppm. $\Delta\nu_{1/2}$ = 307 Hz.

Data for $Ph_3GeOTcO_3$. Yield: 90% (42 mg). IR (ν in cm^{-1}): 3070 (w), 2963 (w), 1481 (w), 1427 (m), 1308 (w), 1261 (m), 1096 (s), 1022 (m), 937 (s), 895 (m), 806 (s), 737 (s), 694 (s), 459 (s). ^{99}Tc NMR (THF): δ 25.2 ppm. $\Delta\nu_{1/2}$ = 374 Hz.

Data for $(THF)Ph_3SnOTcO_3$. Yield: 92% (54 mg). Anal. Calcd for $C_{22}H_{23}O_5SnTc$: Tc, 16.8. Found: Tc, 15.8. IR (ν in cm^{-1}): 3429 (w), 3067 (w) 3020 (w), 2966 (w), 1481 (w), 1427 (m), 1261 (w), 1076 (w), 1022 (w), 999 (w), 941 (st), 887 (st), 845 (st), 729 (m), 694 (m) 448 (m). ^{99}Tc NMR (THF): δ −5.1 ppm. $\Delta\nu_{1/2}$ = 237 Hz. ^{119}Sn NMR (THF): δ −110.1 ppm $\Delta\nu_{1/2}$ = 241 Hz.

Data for $Ph_3PbOTcO_3$. Yield: 86% (51 mg). IR (ν in cm^{-1}): 3051 (w), 2963 (w), 1566 (w), 1474 (w), 1427 (m), 1327 (w), 1096 (m), 1061 (m), 1018 (m), 995 (m), 930 (s), 891 (s), 802 (s), 721 (s) 687 (s), 436 (m). ^{99}Tc NMR (THF): δ 7.0 ppm. $\Delta\nu_{1/2}$ = 102 Hz. ^{99}Tc elemental analyses show too low values for this compound. This is mainly due to absorption of a significant quantity of the weak β^- radiation by the lead atom, which is only about 4 Å apart from the technetium atom during measurements with this radiometric method.

Syntheses of $[(O_3TcO)Sn^tBu_2(OH)]_2$. $AgTcO_4$ (0.2 mmol) was suspended in 5 mL of dry THF, and 0.1 mmol of $^tBu_2SnCl_2$ was added. The mixture was stirred for 2 h at room temperature and the precipitated AgCl removed by filtration. The solution was reduced under vacuum to 1.5 mL and stored at −20 °C for 1 day. $[(O_3TcO)Sn^tBu_2(OH)]_2$ was obtained as colorless crystals. Upon further concentration of the solution, more substance of the compound was obtained as a colorless powder.

Data for $[(O_3TcO)Sn^tBu_2(OH)]_2$. Yield: 15% (15 mg). ^{99}Tc NMR (THF): δ −2.5 ppm. $\Delta\nu_{1/2}$ = 293 Hz. ^{119}Sn NMR (THF): no signal.

Syntheses of $[(THF)_4Mg(OTcO_3)_2]$. $AgTcO_4$ (0.1 mmol) was suspended in 3 mL of dry THF, and 0.2 mmol of PhMgCl was added. The mixture was stirred for 2 h at room temperature and the precipitated AgCl removed by filtration. The solution was reduced under vacuum until dryness, washed with benzene, and recrystallized from THF. $[(THF)_4Mg(OTcO_3)_2]$ was obtained as colorless crystals.

Data for $[(THF)_4Mg(OTcO_3)_2]$. Yield: ca. 32% (20 mg). ^{99}Tc NMR (THF): δ −38.0 ppm. $\Delta\nu_{1/2}$ = 120 Hz.

Syntheses of $[TcOCl_3(OH_2)(THF)]$. $AgTcO_4$ (0.1 mmol) was suspended in 3 mL of dry THF, and 4.7 mmol (1 mL) of $^iPr_3SiCl$ was added. The mixture was stirred for 2 h at room temperature and the precipitated AgCl removed by filtration. The solvent was removed under vacuum and the obtained oil recrystallized from a THF/acetonitrile mixture. $[TcOCl_3(OH_2)(THF)]$ was obtained upon standing for 3 weeks as extremely moisture-sensitive, large yellow crystals. Yield: ca. 50% (23 mg).

X-ray Crystallography. The intensities for the X-ray determinations were collected on a STOE IPDS 2T instrument with Mo Kα radiation (λ = 0.710 73 Å) at 200 K. Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with *SHELXS97* and *SHELXL97*.[23] Hydrogen atom positions were calculated for idealized positions and treated with the "riding model" option of *SHELXL*, if not mentioned otherwise. More details on data collections and structure calculations are contained in Table 6. Additional information on the structure determinations has been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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Supporting Information Available: X-ray crystallographic data in CIF format and ^{99}Tc NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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