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Article

Technetium Tetrachloride as A Precursor for Small Technetium(IV) Complexes

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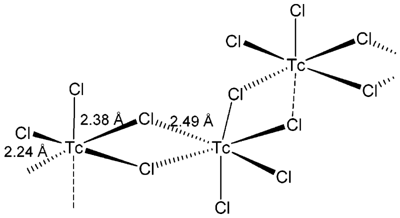
Polymeric technetium tetrachloride reacts with monodentate donor ligands such as THF, acetonitrile, DMSO, thioxane (1-oxa-4-thiacyclohexane), PMe_2Ph, PPh_3, $OPPh_3$, or OH_2 via cleavage of the polymeric network and the formation of $[TcCl_4(L)_2]$ complexes. The configuration of the products is dependent on the donor atoms such that trans coordination is established with 'soft' donor atoms such as sulfur or phosphorus, while *cis*-$[TcCl_4(L)_2]$ complexes are formed with the 'harder' donors oxygen or nitrogen. The ambivalent thioxane binds to technetium via the sulfur atom. The trans products are air stable and resistant to hydrolysis. The cis complexes, however, undergo stepwise hydrolysis, during which complexes of the composition $[Cl_3(L)_2TcOTc(L)_2Cl_3]$ (L = CH_3CN, DMSO, or OH_2) are formed. They are the first representatives of a new class of technetium(IV) complexes with a bridging oxo ligand. The Tc–O bond lengths in these bridges are between 1.803(1) and 1.823(2) Å.

Introduction

The oxidation state '+4' is one of the most stable for technetium, but its coordination chemistry is scarcely explored.[1] The $4d^3$ electronic configuration of the Tc(IV) complexes implies a 'borderline' situation, which lies between that of complexes stabilized by π-donors and π-acceptors. Technetium(IV) complexes often tend to hydrolyze or to form polymeric compounds. This also holds true for the most common Tc(IV) starting materials, the $[TcX_6]^{2-}$ (X = Cl, Br, I) complexes. They hydrolyze under final formation of the polymeric '$TcO_2 \cdot nH_2O$'.[1−5] Ligand-exchange reactions starting from hexahalotechnetates often yield mixtures of products.

A hitherto rarely used Tc(IV) starting material is the neutral technetium tetrachloride. The dark red compound crystallizes as polymeric chains, in which the Tc atoms are bridged by chloro ligands giving edge-sharing, distorted octahedra (**1**) with three distinct Tc−Cl bond lengths.[6a] The longest one (2.49 Å) is associated with the bridging chlorine atoms perpendicular to the chain. These bonds should be easily cleaved by donor solvents and yield *cis*-$[TcCl_4(L)_2]$ complexes, as was concluded from spectroscopic data in reactions with acetonitrile and isocyanides in an early report.[6b] Very recently, we could isolate *cis*-$[TcCl_4(CH_3CN)_2]$ (**2**) in crystalline form and elucidate its crystal structure.[7]



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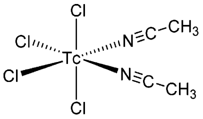

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The ready availability of **2** and its potential as a precursor in Tc(IV) chemistry prompted us to study reactions of $(TcCl_4)_n$ with other donor solvents such as THF, DMSO, and dioxane, or simple, monodentate ligands such as PPh_3, PMe_2Ph, $OPPh_3$, or thioxane (1-thia-4-oxa-cyclohexane).

Experimental Section

General Considerations. All reactions were performed using standard Schlenk technique. Solvents were analytical grade, flushed with argon, and carefully dried prior to use. $(TcCl_4)_n$ was prepared from Tc metal and Cl_2 following the standard procedure of Colton.[8] Particular care was taken to avoid any breakthrough of volatile radioactive material by several washings of the exhausting gas stream with aqueous KOH solution.

IR spectra between 400 and 4000 cm^{-1} were measured as KBr pellets on a Shimadzu FTIR spectrometer. Far IR measurements were done in Nujol using polyethylene windows on a Nicolet Nexus FTIR spectrometer. Raman spectra were measured on a Bruker RFS 100/S spectrometer. Technetium elemental analyses were done by liquid scintillation measurements.

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

***cis*-[TcCl$_4$(CH$_3$CN)$_2$] (2).** The synthesis of **2** is reported elsewhere.[7] Elemental analysis of the solvent-free sample: $C_4H_6N_2Cl_4Tc$ (322.9); Tc, 29.9 (calcd 30.7)%. Raman (ν_{max}/cm^{-1}): 2313, 2288 (C≡N); 369, 322 (Tc−Cl).

***cis*-[TcCl$_4$(THF)$_2$] (3).** $(TcCl_4)_n$ (0.1 mmol, 24 mg) was suspended in 2 mL of carefully dried THF and heated at reflux for 2 h. The obtained green solution was reduced in volume to 1 mL and kept at −20 °C overnight, giving yellow crystals. Yield: 17 mg, 44%. Elemental analysis: $C_8H_{16}O_2Cl_4Tc$ (385.0); Tc, 25.4 (calcd 25.7)%. IR (ν_{max}/cm^{-1}): 364, 348 (Tc−Cl).

***cis*-[TcCl$_4$(OH$_2$)$_2$]·2dioxane (4·2dioxane).** The synthesis of the compound is described in ref 7. Technetium analysis did not give satifactory values due to partial decomposition of the isolated crystals upon drying. IR (ν_{max}/cm^{-1}): 360, 339 (Tc−Cl), 436 (Tc−O), 2870 (O−H).

***cis*-[TcCl$_4$(OPPh$_3$)$_2$] (5).** $(TcCl_4)_n$ (0.1 mmol, 24 mg) was dissolved in 2 mL of THF, and $OPPh_3$ (0.2 mmol, 56 mg) was added. The mixture was stirred at room temperature for 2 h. Reduction of the volume of the resulting dark green solution to 1 mL and standing overnight gave large greenish-yellow crystals (21 mg, 30%). More of the product was recovered by further concentration of the mixture in a vacuum as a microcrystalline solid. Overall yield: 63 mg, 90%. Elemental analysis: $C_{36}H_{30}O_2P_2Cl_4Tc$ (797.4); Tc, 12.2 (calc. 12.4)%. IR (ν_{max}/cm^{-1}): 350, 336 (Tc−Cl), 1122 (O═P).

***trans*-[TcCl$_4$(thioxane)$_2$] (6).** $(TcCl_4)_n$ (0.1 mmol, 24 mg) was suspended in 2 mL of neat thioxane. Stirring at room temperature for 2 h resulted in the formation of a clear red solution. The reaction mixture was halved in volume and placed overnight in a refrigerator. Dark red crystals were obtained. Yield: 30 mg, 60%. Elemental analysis: $C_8H_{16}O_2S_2Cl_4Tc$ (449.2); Tc, 21.9 (calc. 22.0)%. IR (ν_{max}/cm^{-1}): 352, 344 (Tc−Cl), 264 (Tc−S).

***trans*-[TcCl$_4$(PPh$_3$)$_2$] (7).** $(TcCl_4)_n$ (0.1 mmol, 24 mg) was dissolved in 2 mL of THF, and PPh_3 (0.2 mmol, 52 mg) was added. The mixture was stirred at room temperature for 2 h. During this time, the product precipitated as a sparingly soluble, green powder. Yield: 57 mg, 75%. The spectroscopic and analytical data are identical with those previously reported for **7**.[9]

Reaction of (TcCl$_4$)$_n$ with PMe$_2$Ph. Reactions of $(TcCl_4)_n$ with PMe_2Ph gave the same products as were obtained starting from $[TcCl_6]^{2-}$.[10] This means the addition of 2 equiv of the phosphine to a suspension of the tetrachloride in benzene and stirring at room-temperature resulted in a slow dissolution of $(TcCl_4)_n$ and the formation of a clear, dark green solution, from which *trans*-$[TcCl_4(PMe_2Ph)_2]$ (**8**) could be isolated in almost quantitative yield. The use of a 10-fold excess of PMe_2Ph resulted in the reduction of technetium, and the orange-red *mer*-$[TcCl_3(PMe_2Ph)_3]$ (**9**) was isolated in a yield of 80%.

The well-known complexes were characterized by their IR spectra and elemental analyses and compared with literature values. *mer*-$[TcCl_3(PMe_2Ph)_3]$ was additionally characterized by the determination of the unit cell dimensions of the obtained single crystals (monoclinic, $a = 10.935$ Å, $b = 39.191$ Å, $c = 13.738$ Å, $\beta = 107.3°$), which were identical with the previously published values.[10]

[{TcCl$_3$(CH$_3$CN)$_2$}$_2$O] (10). The synthesis was performed as described for **2**, but after the complete dissolution of $(TcCl_4)_n$, the mixture was exposed to air. After 1 day, golden-brown crystals deposited. Yield: almost quantitative. Elemental analysis: $C_8H_{12}N_4OCl_6Tc_2$ (590.9); Tc, 33.2 (calcd 33.5)%. IR (ν_{max}, cm^{-1}) 2318, 2291 (C≡N); Raman (ν_{max}/cm^{-1}): 340 (Tc−Cl), 2316, 2292 (C≡N).

[{TcCl$_3$(OH$_2$)$_2$}$_2$O]·6dioxane (11·6dioxane). (a) $(TcCl_4)_n$ (24 mg, 0.1 mmol) was dissolved in 3 mL of dioxane, which was not dried prior use, and the mixture was stirred at room temperature for 3 h. The volume of the resulting dark green solution was reduced in a vacuum to about 1 mL. Golden-brown crystals precipitated upon standing overnight at room temperature. Yield: 33 mg, 65%. (b) Alternatively, the dioxane solution of **4** was exposed to air. The color of the solution changed from dark green to brown, and single crystals of **11**·6dioxane could be recovered after concentration. Yield: 28 mg, 55%. IR (ν_{max}, cm^{-1}): 798 (Tc−O−Tc), 375, 351 (Tc−Cl), 575, 472 (Tc−O_{water}), 2858 (O−H, H-bonded). Technetium analysis did not give satisfactory results due to partial decomposition of the isolated crystals upon drying.

[{TcCl$_3$(DMSO)$_2$}$_2$O] (12). $(TcCl_4)_n$ (24 mg, 0.1 mmol) was dissolved in 1 mL of dried DMSO and exposed to air. After 1 day, green crystals of **12** appeared. Yield: 15 mg, 20%. Elemental analysis: $C_8H_{24}Cl_6O_5S_4Tc_2$ (739.2); Tc, 26.9 (calcd 26.8)%. IR (ν_{max}/cm^{-1}): 890 (S═O), 352, 344 (Tc−Cl).

[{TcCl$_3$(DMSO)$_3$]$_2$[TcCl$_6$] (13). (a) $(TcCl_4)_n$ (24 mg, 0.1 mmol) was dissolved in 1 mL of dried DMSO. The resulting green mixture was treated with 4 mL of acetonitrile, which resulted in a color change to yellow-green, and yellow crystals of **13** precipitated upon standing overnight at room temperature. Yield: 56 mg, 47%. (b) The same product could be isolated from the reaction between *trans*-$[TcCl_4(PPh_3)_2]$ and DMSO after the addition of acetonitrile as

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Table 1. X-ray Structure Data Collection and Refinement Parameters

	cis-[$TcCl_4(THF)_2$] (**3**)	*cis*-[$TcCl_4(OPPh_3)_2$] (**5**)	*trans*-[$TcCl_4(thioxane)_2$]· thioxane (**6**·thioxane)	[{$TcCl_3(CH_3CN)_2$}$_2$O] (**10**)	[{$TcCl_3(DMSO)_2$}$_2$O] (**11**)[c]	[{$TcCl_3(DMSO)_3$}]$_2$-[$TcCl_6$](**13**)
formula	$C_8H_{16}Cl_4O_2Tc$	$C_{36}H_{30}Cl_4O_2P_2Tc$	$C_{12}H_{24}Cl_4O_3S_3Tc$	$C_8H_{12}Cl_6N_4OTc_2$	$C_8H_{24}Cl_6O_5S_4Tc_2$	$C_{12}H_{36}Cl_{12}O_6S_6Tc_3$
M_w	385.01	797.34	553.29	590.92	739.21	1191.17
cryst syst	orthorhombic	monoclinic	triclinic	hexagonal	monoclinic	triclinic
a/Å	7.737(1)	13.896(1)	6.470(1)	10.072(1)	11.335(2)	8.703(1)
b/Å	12.658(2)	12.993(1)	6.469(1)	10.072(1)	9.463(1)	8.968(1)
c/Å	13.941(1)	19.412(2)	12.831(3)	44.724(2)	13.116(2)	13.909(2)
α/°	90	90	93.95(2)	90	90	104.28(1)
β/°	90	95.82(1)	93.87(2)	90	113.13(1)	100.53(1)
γ/°	90	90	104.46(2)	120	90	93.59(1)
V/Å^3	1365.4(2)	3486.7(5)	516.8(2)	3929.1(2)	1293.8(3)	1027.7(3)
space group	$P2_12_12_1$	$C2/c$	$P\bar{1}$[b]	$P6_122$	$P2/c$	$P\bar{1}$
Z	4	4	1	6	2	1
D_{calcd}/g cm^{-3}	1.868	1.517	1.775	1.493	1.892	1.920
μ/mm^{-1}	1.816	0.843	1.524	1.667	2.026	2.106
no. of reflns	4482	12 299	5348	56 221	2095	6136
no. independent reflns	3086	4661	2737	2795	2095	3248
no. params	137	204	116	98	114	178
R1/wR2[a]	0.0518/0.1425	0.0450/0.1166	0.0390/0.1046	0.0466/0.1206	0.0969/0.2701	0.0609/0.1529
GOF/Flack	1.037/−0.05(7)	0.858/−	0.796/−	1.091/0.1(1)	0.953/−	1.040/−
temp/K	173	200	200	200	200	200
CCDC ref	CCDC 613257	CCDC 613258	CCDC 613259	CCDC 613260	CCDC 613261	CCDC 613262

[a] $R1 = \sum(|F_o - F_c|)/\sum|F_o|$ for observed reflections; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^2)]^{-1/2}$ for all reflections. [b] The structure of the complex can also be refined in the higher symmetric space group $C2/m$. This results, however, in lower R values since the disordered solvent thioxane does not fit this space group. [c] Poor crystal quality and some twinning give comparably high R values.

described before.[11] Elemental analysis: $C_{12}H_{36}O_6S_6Cl_{12}Tc_3$ (1191.2); Tc, 25.3 (calcd 24.9)%. IR (ν_{max}/cm^{-1}): 895 (S=O), 353, 340 (Tc−Cl).

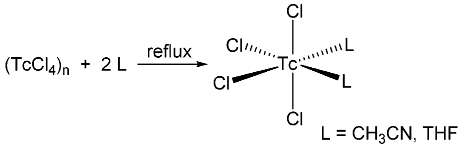
X-ray Crystallography. The intensities for the X-ray determinations were collected on a STOE IPDS 2T instrument with Mo Kα radiation ($\lambda = 0.71073$ Å). Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with SHELXS97 and SHELXL97.[12] Hydrogen atom positions were calculated for idealized positions and treated with the ‘riding model’ option of SHELXL, except of those H-atoms bonded to nitrogen atoms and/or involved in hydrogen bonds. Their positions were derived from the final Fourier maps and refined. More details on data collections and structure calculations are contained in Table 1.

Additional information on the structure determinations have been deposited with the Cambridge Crystallographic Data Centre.

Results and Discussion

The red, neutral technetium tetrachloride readily dissolves in a series of donor solvents and forms neutral Tc(IV) complexes of the composition [$TcCl_4(L)_2$] (Scheme 1). The products can be isolated as crystalline solids when the presence of water is strictly avoided during all manipulations. Recently, this has been successfully demonstrated for the reaction with acetonitrile, and the crystal structure of the resulting **2** was reported in a preliminary communication.[7] **2** is a yellow solid, which is stable in dry air. Traces of moisture, however, result in a progressive darkening of the large crystals and slow hydrolysis. The formation of the cis product is not unexpected in light of the solid-state structure of the polymeric **1**. It corresponds with the cleavage of the longest (weakest) Tc−Cl bonds in **1** and the occupation of the vacant coordination positions by the donor solvent.

Scheme 1



The general trend of this reaction is confirmed when **1** is dissolved in THF. Yellow crystals of **3** deposit from the obtained green solution upon standing overnight in a refrigerator. The compound is extremely moisture-sensitive and decomposes on contact with moist air under formation of a brownish, oily product. In dry air, **3** is stable and can be stored without decomposition. The moisture sensitivity is unlike the behavior of the analogous rhenium(IV) complex, which is more resistant to moisture and can be handled for a short time in air.[13]

A single-crystal structure analysis of **3** confirms the cis arrangement of the THF ligands. The molecular structure of the compound is shown in Figure 1. Selected bond lengths and angles are compared with the values for other *cis*-[$TcCl_4(L)_2$] complexes in Table 2. The technetium atom possesses an almost perfect octahedral coordination sphere. As is to be expected, two different Tc−Cl bond lengths are observed as a consequence of the corresponding trans ligands. In all cases, the trans-labilizing effect of the chloro ligand is larger than that of the oxygen- or nitrogen-donor ligands. The Tc−N and Tc−O bonds in **2** and **3** are in the typical range of single bonds.[15] Although THF is a common solvent in the synthetic coordination chemistry of technetium, only a few examples exist where this cyclic ether acts as a ligand,[1]

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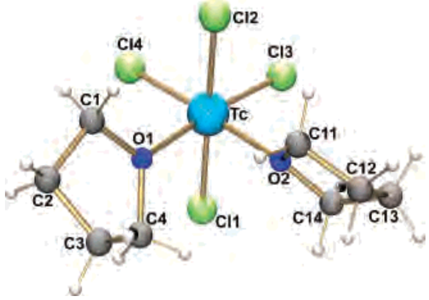


Figure 1. Molecular structure of **3**.[14]

Table 2. Selected Bond Lengths (Å) and Angles (deg) in **3** and **5**[a]

	3	**5**	**2**·CH_3CN[b]	**4**·2dioxane[b]
Tc−Cl1	2.320(1)	2.334(1)	2.323(2)	2.331(2)
Tc−Cl2	2.315(1)	2.334(1)[c]	2.308(2)	2.331(2)[e]
Tc−Cl3	2.286(1)	2.308(1)	2.279(2)	2.283(3)
Tc−Cl4	2.283(1)	2.308(1)[c]	2.279(2)[d]	2.283(3)[e]
Tc−O1/N1	2.111(4)	2.029(3)	2.123(5)	2.096(7)
Tc−O2/N2	2.110(4)	2.029(3)[c]	2.123(5)[d]	2.096(7)[e]
O1/N1−Tc−O2/N2	84.3(2)	88.6(2)[c]	88.1(3)	84.9(5)
Cl1−Tc−Cl2	176.39(5)	174.07(5)[c]	171.09(9)	170.8(1)

[a] The values of the previously published compounds **2** and **4** are given for comparison. The atomic labeling schemes for **2** and **4** are adopted to that of the THF complex in Figure 1. [b] Values taken from ref 7. [c] Symmetry related atoms, symmetry operation: $1 - x, y, -0.5 - z$. [d] Symmetry related atoms, symmetry operation: $x, 1.5 - y, z$. [e] Symmetry related atoms, symmetry operation: $0.5 - x, -0.5 - y, z$.

and **3** is the first example of such a compound which has been studied crystallographically.[15]

The THF ligands in **3** are only weakly bonded, and thus, the complex can be used as a precursor for the synthesis of other Tc(IV) complexes. Addition of 2 equiv of $OPPh_3$ to the yellow solution of **3** in THF results in a green reaction mixture, and greenish-yellow crystals of **5** are obtained after concentration. The compound can be handled in air for some minutes without decomposition. Longer exposure to moisture, however, results in subsequent darkening of the surface of the crystals and slow hydrolysis, which finally gives 'hydrolyzed TcO_2' as an insoluble, almost black solid. The IR band of the $OPPh_3$ ligand is observed at 1122 cm^{-1}. This corresponds to a slight bathochromic shift with respect to the noncoordinated phosphine oxide (1195 cm^{-1}).

The single-crystal structure of **5** confirms the cis coordination of the bulky $OPPh_3$ ligands. A graphical representation of the molecular structure is given in Figure 2. Selected bond lengths and angles are contained in Table 2. All main structural features discussed for **3** are also valid for **5**. It is remarkable that despite the steric bulk of the phosphine oxide ligands the O−Tc−O angle is smaller than 90°. The structural trans influence of $OPPh_3$ is slightly larger than for acetonitrile or THF in the compounds **2** and **3**, respectively. The observed Tc−O bond length in **5** is smaller than the values in the only three previously published complexes of technetium with phosphine oxide ligands. Only one of them, the Tc(II) thionitrosyl compound [Tc(NS)Cl_2(PMe$_2$Ph)(OPMe$_2$Ph)], contains a monodentate phosphine oxide (Tc−O bond length: 2.097 Å).[16a] The NS^+ ligand, however, is known to cause a perceptible trans influence, which explains the observed difference. The other two examples, [$TcCl_2$-{$Ph_2P(O)py$-N,O}$_2$](PF_6) and [$TcCl_2$(dppmO−P,O)$_2$](PF_6) (dppmO = bis(diphenylphosphinomethane monoxide),[16b] contain chelate-bonded phosphine oxides and, hence, are not suitable for comparison.

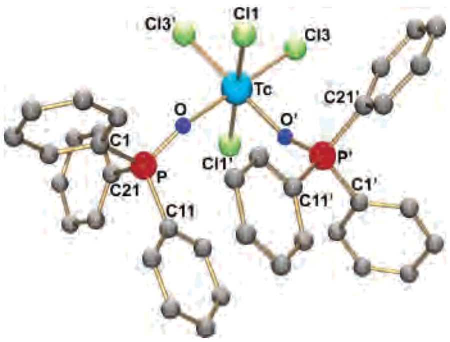
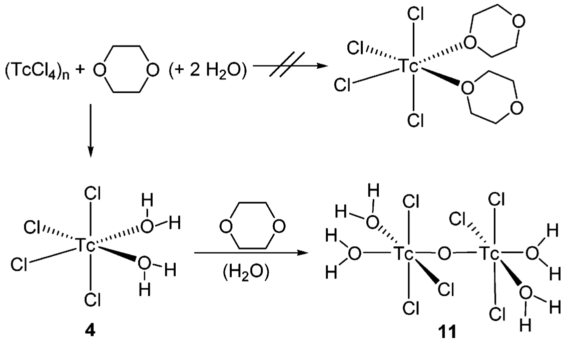


Figure 2. Molecular structure of **5**.[14]

Scheme 2



A completely different reaction pattern was observed for the reaction of $(TcCl_4)_n$ with dioxane. The donor abilities of this cyclic ether were apparently not good enough to stabilize the corresponding *cis*-[$TcCl_4(L)_2$] complex. Instead, the technetium tetrachloride reacted with traces of water, which were present even in carefully dried dioxane (Scheme 2). Details of this hydrolysis have been published before[7] and shall not be outlined here in detail. Isolation of molecular intermediates from aqueous solutions (although suggested by model calculations)[4] has so far failed.

From the stepwise hydrolysis of $(TcCl_4)_n$ in moist dioxane, we were able to isolate two molecular intermediates of this reaction in crystalline form, the monomeric **4**·2dioxane and the oxo-bridged dimer **11**·6dioxane. The unexpected stability of the aqua complexes **4** and **11** is explained by their solid-state structures. Both compounds co-crystallize with dioxane solvate molecules. Hydrogen bonds between the aqua ligands and the surrounding dioxane molecules arrange the complex molecules such that they are completely encapsulated by dioxane. The three-dimensional networks prevent polymerization and the final formation of 'hydrolyzed TcO_2' as long

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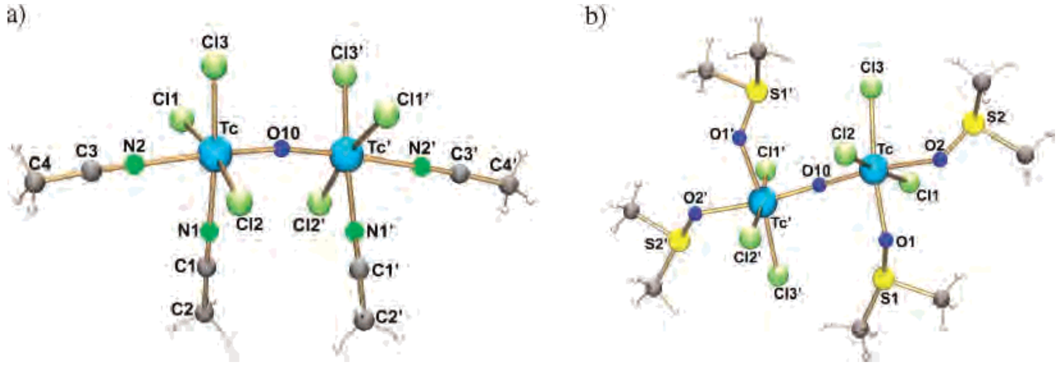

Figure 3. Molecular structures of the oxo-bridged complexes (a) **10** and (b) **12**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in $[TcCl_3(L)_2OTcCl_3(L)_2]$ Complexes[a]

	10[b]	**12**[c]	**11**[d,e]
Tc−Cl1	2.346(2)	2.384(5)	2.344(2)
Tc−Cl2	2.341(2)	2.344(5)	2.346(2)
Tc−Cl3	2.307(2)	2.340(5)	2.317(2)
Tc−O10	1.803(1)	1.823(2)	1.812(1)
Tc−N1/O1	2.128(6)	2.06(1)	2.116(4)
Tc−N2/O2	2.135(5)	2.12(1)	2.132(3)
O10−Tc−N2/O2	176.6(2)	172.7(4)	178.67(9)
Tc−O10−Tc′	171.8(3)	168.3(9)	180

[a] The atomic labeling scheme for **11** is adopted to that of the other complexes. [b] Symmetry related atoms, symmetry operation: x, $x - y$, $1/6 - z$. [c] Symmetry related atoms, symmetry operation: $2 - x$, y, $3/2 - z$. [d] Symmetry related atoms, symmetry operation: $1 - x$, $-y$, $1 - z$. [e] Values taken from ref 7.

as the compounds are stored under dioxane. In air, however, the single crystals rapidly decompose under formation of an oily residue. The same type of decomposition was observed during attempts to obtain pure samples for elemental analysis by drying the crystals in a vacuum. We have not yet been able to isolate defined oxo-bridged compounds with more than two technetium atoms.

The formation of oxo-bridged technetium(IV) dimers is not restricted to the hydrolysis product of the aqua complex described above. Reactions of moist acetonitrile or DMSO with $(TcCl_4)_n$ also results in a partial hydrolysis of the intermediately formed *cis*-$[TcCl_4(L)_2]$ complexes. This is indicated by a subsequent darkening of the yellow-green reaction mixtures and the formation of golden-brown precipitates. The corresponding reaction with acetonitrile is almost quantitative and yields **10** as compact single crystals, while the analogous reaction mixture with DMSO must be concentrated almost to dryness to yield **12** as thin crystal plates. The IR and Raman spectra of the products agree with the structures of **10** and **12**. They show Tc−Cl bands between 340 and 355 cm^{-1} and the C≡N vibrations of **10** are detected as strong bands at 2316 and 2292 cm^{-1}. Figure 3 illustrates the molecular structures of the dimeric complexes **10** and **12**. Selected bond lengths and angles are summarized in Table 3 and compared with the values in the previously published aqua complex, **11**. Oxo bridges are common in the coordination chemistry of technetium(V), where the almost linear $[O{=}Tc{-}O{-}Tc{=}O]^{4+}$ core is perfectly suitable for the stabilization of neutral complexes with bidentate, monoanionic or tetradentate, dianionic ligands.[1] The bonding situation in such compounds is characterized by a considerable electron donation from the p_x and p_y orbitals of the oxygen atom to d_π orbitals of the metal ions. This is mainly indicated by the relatively short Tc−O−Tc bonds. The same holds true for the bridging oxygen ligands in **10**, **11**, and **12**. With values between 1.803(1) and 1.823(2) Å, these bond lengths are between those expected for common Tc−O single and double bonds. The Tc−O−Tc bond angles are essentially linear with angles between 168.3(9)° and 180°. The structural trans influence due to the bridging oxo ligands is slightly larger than that of a chloro ligand. Compounds **10**, **11**, and **12** represent the first examples of complexes with an oxygen bridge between two Tc(IV) centers. Structural information about similar systems were hitherto restricted to complexes of Tc(V),[17] Tc(III),[18] and some mixed-valent complexes, which also contain bridging oxo ligands.[19]

Complex **12** is the first technetium complex with oxygen-bonded DMSO ligands to be studied by X-ray crystallography. Its isolation in crystalline form from neat DMSO was successful due to its relatively low solubility in this solvent. Up to now, we have not been able to isolate single crystals of its 'parent complex' *cis*-$[TcCl_4(DMSO)_2]$, but we have no doubt that this compound exists in the yellow solution, which is formed after the dissolution of $[TcCl_4]_n$ in dry DMSO. The synthesis of this neutral, monomeric complex was described in a previous paper by the reaction of *trans*-$[TcCl_4(PPh_3)_2]$ with DMSO in boiling acetonitrile and subsequent precipitation of the product as a yellow powder with a large excess of diethyl ether.[11] The compound was characterized by elemental analysis, IR, and NMR spectroscopy. Main support for its composition comes from FAB^+ mass spectrometry in nitrobenzyl alcohol (NBA), where the molecular ion of $[TcCl_4(DMSO)_2(NBA)]^+$ was registered at $m/z = 548$ with the correct isotopic pattern for

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(17) (a) Bandoli, G.; Nicolini, M.; Mazzi, U.; Refosco, F. *J. Chem. Soc., Dalton Trans.* **1984**, 2505. (b) Baldas, J.; Colmanet, S. F.; Mackay, M. F. *J. Chem. Soc., Dalton Trans.* **1988**, 1725. (c) Tisato, F.; Refosco, F.; Mazzi, U.; Bandoli, G.; Dolmella, A. *Inorg. Chim. Acta*, **1989**, *164*, 127. (d) Pillai, M. R. A.; John, C. S.; Lo, J. M.; Schlemper, E. O.; Troutner, D. E. *Inorg. Chem.* **1990**, *29*, 1850. (e) Pietzsch, H.-J.; Spies, H.; Leibnitz, P.; Reck, G.; Beger, J.; Jacobs, R. *Polyhedron*, **1993**, *12*, 187. (f) Abram, U.; Abram, S.; Mäcke, H. R.; Koch, P. *Z. Anorg. Allg. Chem.* **1995**, *621*, 854.

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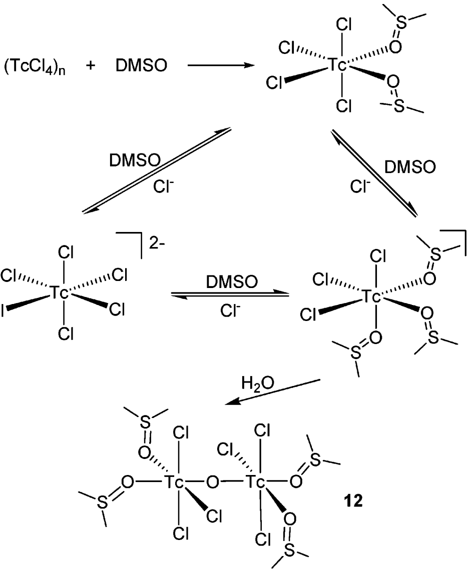
(19) (a) Kastner, M. E.; Fackler, P. H.; Podbielski, L.; Chakoudian, J.; Clarke, M. J. *Inorg. Chim. Acta* **1986**, *114*, 11. (b) Clarke, M. J.; Kastner, M. E.; Podbielski, L. A.; Fackler, P. H.; Schreifels, J.; Meinken, G.; Srivastava, S. C. *J. Am. Chem. Soc.* **1988**, *110*, 1818.

Scheme 3



four chloro ligands. Our attempts to obtain crystalline $[TcCl_4(DMSO)_2]$ by layering acetonitrile/diethyl ether over a DMSO solution of $[TcCl_4(DMSO)_2]$ resulted in the precipitation of single crystals of the ionic compound **13**. Single crystals of the same composition were also obtained from the $[TcCl_4(PPh_3)_2]$/DMSO/CH_3CN reaction mixture described above.[11] Obviously, the DMSO ligands are only weakly bonded to technetium and an equilibrium is established, which involves species such as $[TcCl_3(DMSO)_3]^+$ and $[TcCl_6]^{2-}$ ions (Scheme 3). Addition of acetonitrile then results in the separation of single crystals of the ion pair **13**, while the dimeric compound **12** is formed after diffusion of water into such solutions. Interestingly, no ligand-exchange products with the donor solvent acetonitrile were identified during these manipulations.

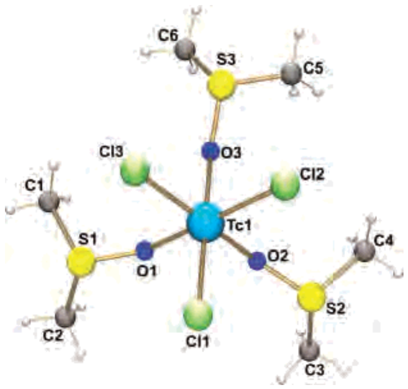


Figure 4. Molecular structure of the complex cation in **13**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in the Complex Cation of **13**

Tc1−Cl1	2.304(3)	Tc1−O1	2.036(7)
Tc1−Cl2	2.304(3)	Tc1−O2	2.035(7)
Tc1−Cl3	2.309(3)	Tc1−O3	2.053(6)
O1−S1	1.558(6)	O2−S2	1.560(6)
O3−S3	1.544(8)		
Cl1−Tc1−Cl2	93.4(1)	Cl1−Tc1−Cl3	93.4(1)
Cl1−Tc1−O1	90.9(2)	Cl1−Tc1−O2	92.0(2)
Cl1−Tc1−O3	173.9(2)	Cl2−Tc1−Cl3	93.8(1)
Cl2−Tc1−O1	173.8(2)	Cl2−Tc1−O2	92.0(2)
Cl2−Tc1−O3	90.9(2)	Cl3−Tc1−O1	90.4(2)
Cl3−Tc1−O2	171.9(2)	Cl3−Tc1−O3	90.7(2)
O1−Tc1−O2	83.4(3)	O1−Tc1−O3	84.5(3)
O2−Tc1−O3	83.5(3)		

Scheme 4

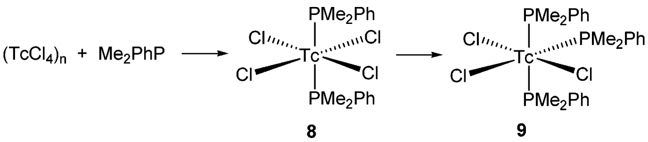


Figure 4 contains the molecular structure of the complex cation of **13** with three DMSO ligands in facial arrangement. Since the $[TcCl_6]^{2-}$ anions have the expected octahedral structure and no intermolecular contacts are established between the ion pairs, the counterions have been omitted for clarity. Table 4 contains selected bond lengths and angles. The Tc−O and Tc−Cl bond lengths show no unusual features, but it is remarkable that the coordination octahedron is distorted such that the angles between the facially coordinated DMSO ligands are considerably smaller than 90°. The same feature is observed in the solid-state structure of **12**, where the O1−Tc−O2 angle of 82.3(5)° can be explained by a partial double-bond character of the trans-situated Tc−O bond. In **13**, however, the DMSO ligands are trans to chloro ligands, which does not explain the observed distortion. A possible explanation may be weak interactions between the oxygen atoms, leading to interatomic distances between 2.709 and 2.759 Å, which is shorter than the sum of the van der Waals radii. Markedly longer metal−oxygen distances (3.165−3.213 Å) are observed in another second-row transition metal complex with a $\{MCl_3(DMSO)_3\}$ coordination sphere, the polymeric $[\{(CdCl_2)_5(DMSO)_7\}_n]$,[20] while shorter M−O bonds are observed in a series of hexakis DMSO complexes of first-row transition elements.[15b]

All of the reactions of $(TcCl_4)_n$ with the nitrogen and oxygen donor atom ligands OH_2, THF, DMSO, or $OPPh_3$ discussed above result in the formation of *cis*-$[TcCl_4(L)_2]$ products. This can be understood from the polymeric structure of technetium tetrachloride, which provides two cis positions for coordination after cleavage of the longest Tc−

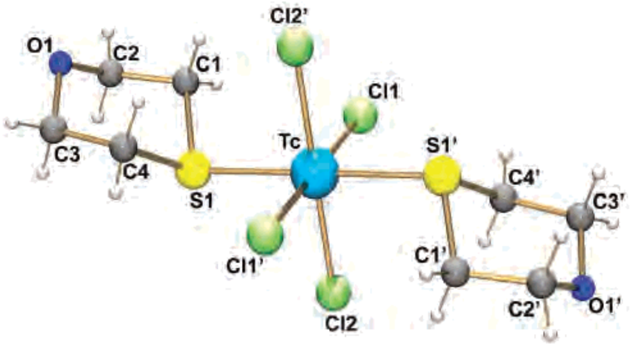


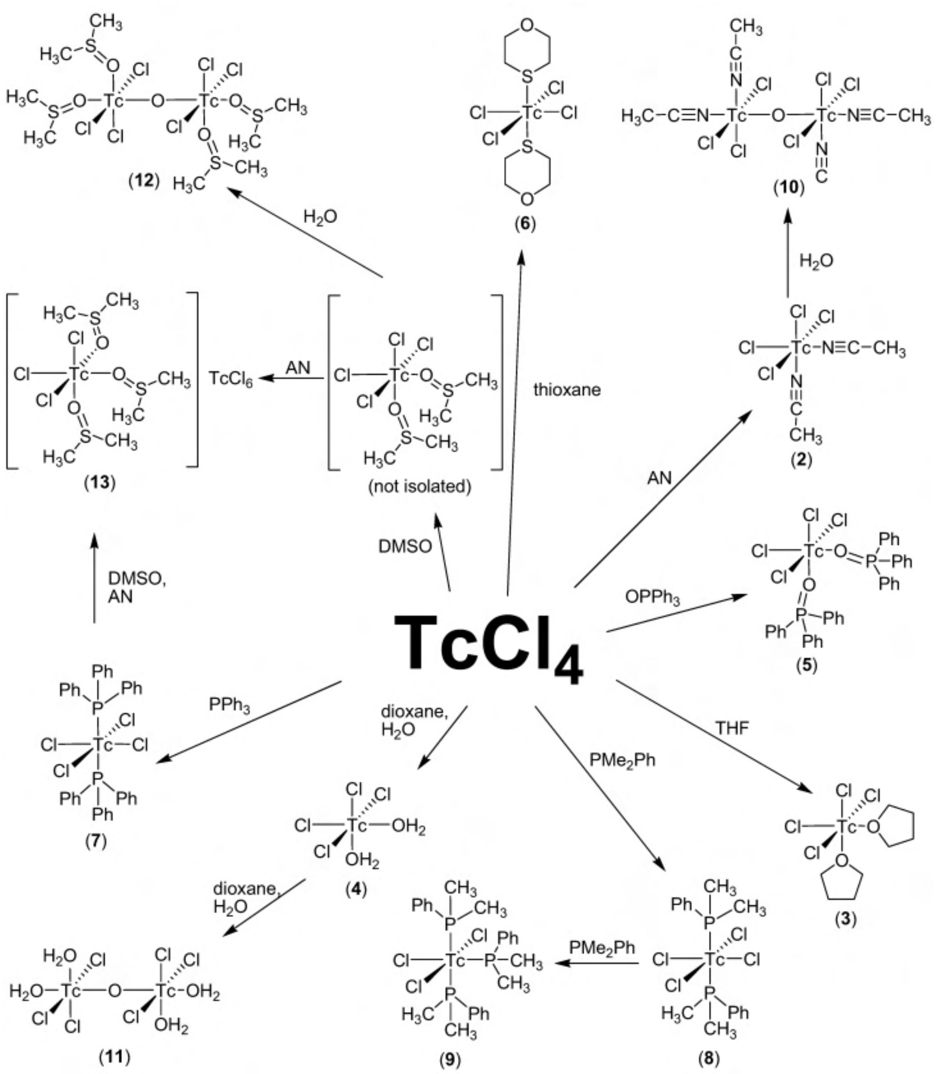
Figure 5. Molecular structure of complex **6**.

Table 5. Selected Bond Lengths (Å) and Angles (deg) in **6**

Tc−Cl1	2.320(1)	Tc−S1	2.476(1)
Tc−Cl2	2.239(0)		
Cl1−Tc−Cl2	89.95(4)	Cl1−Tc−S1	90.01(4)
Cl2−Tc−S1	90.9(2)	Cl1−Tc−Cl2′[a]	90.05(4)

[a] Symmetry related atoms, symmetry operation: (′) 1 − *x*, −*y*, −*z*.

Scheme 5



Cl bonds of the polymer. Nevertheless, a trans arrangement of the incoming ligands is observed with phosphorus or sulfur donor ligands such as PPh_3, Me_2PhP, or thioxane.

A dark green powder begins to precipitate immediately after the addition of PPh_3 to a solution of $(TcCl_4)_n$ in THF. This product was identified as the well-known **7**, which can alternatively be prepared from $[TcCl_6]^{2-}$ or $[TcO_4]^-$/HCl mixtures.[9,10] A similar reaction course is observed with Me_2PhP, which results in the formation of the green **8** when 2 equiv of the phosphine are used, while reduction and formation of the orange-red **9** are observed with an excess of Me_2PhP (Scheme 4). This behavior is not completely unexpected in light of reactions of various Tc(VII), Tc(V), and Tc(IV) precursors with tertiary phosphines,[1,9,10] but in contrast to the formation of the cis adducts, formed with ligands having 'hard' donor atoms (vide supra).

The cyclic ether/thioether 1-oxa-4-thiacyclohexane (thioxane) provides a 'soft' sulfur donor atom and a 'hard' oxygen donor and principally allows for the formation of both isomers depending on the donor atom involved (also bearing in mind that no direct coordination with dioxane was observed in the corresponding experiments). Stirring of $(TcCl_4)_n$ in neat thioxane at room-temperature results in the formation of a clear red solution, from which red crystals of **6** can be isolated upon concentration and cooling. In contrast to the cis complexes described above, **6** is stable even in moist air and no further reactions, e.g., the formation of oxo-bridged dimers, were observed. The compound is soluble in common organic solvents such as benzene or chloroform. The trans coordination of the two thioether ligands was confirmed by X-ray crystallography. Figure 5 shows the molecular structure of **6**. Selected bond lengths and angles are summarized in Table 5. The technetium atom is located on a center of inversion, and its coordination environment can be described as an almost perfect octahedron. Thus, the structure of **6** is very similar to that of *trans*-$[TcCl_4(THT)_2]$ (THT = tetrahydrothiophene), which has been prepared recently from $K_2[TcCl_6]$.[21] It must be noted that attempts to obtain **6** by an analogous reaction between K_2TcCl_6 and thioxane failed and gave only intractable dark-brown oils,

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(20) Nieuwenhuyzen, M.; Wilins, C. J. *J. Chem. Soc., Dalton Trans.* **1993**, 2673.

(21) Hagenbach A.; Abram, U. *Inorg. Chem. Commun.* **2004**, *7*, 1142.

while $(TcCl_4)_n$ reacts with THT in benzene under formation of the known adduct *trans*-$[TcCl_4(THT)_2]$.

Conclusions

The polymeric $(TcCl_4)_n$ is an excellent precursor for the synthesis of small technetium(IV) molecules. Its versatility and the fact that different classes of Tc(IV) complexes can be prepared by simple reactions with common donor solvents justify the relatively cumbersome synthesis of technetium tetrachloride by chlorination of the metal. Scheme 5 represents a summary of the products, which were obtained by direct or subsequent reactions starting from $(TcCl_4)_n$.

$(TcCl_4)_n$ reacts by well-defined procedures with dry solvents having 'hard' donor atoms such as acetonitrile or THF to form *cis*-$[TcCl_4(L)_2]$ complexes, which can be isolated as crystalline solids. Such products are promising candidates as precursors for further ligand exchange reactions with chelating ligands since they are more stable than $(TcCl_4)_n$ but much more reactive than other Tc(IV) precursors such as the sparingly soluble *trans*-$[TcCl_4(PPh_3)_2]$ or salts of the $[TcCl_6]^{2-}$ anion. Such reactions are currently under study in our laboratory and may contribute to the further exploration of the hitherto relatively undexplored coordination chemistry of Tc(IV).

A new class of Tc(IV) complexes having the $\{Tc-O-Tc\}^{6+}$ core is obtained by partial hydrolysis of the *cis*-$[TcCl_4(L)_2]$ compounds. The stability of the oxo-bridged complexes is dependent on the incoming ligands. While the corresponding acetonitrile compound **10** is mostly stable against further hydrolysis and can be stored in air for a few hours without decomposition, the corresponding aqua compound **11** is only stable in a matrix of hydrogen-bonded dioxane solvents molecules, which keep the complex molecules apart from each other thus preventing further hydrolysis and the final formation of $TcO_2 \cdot nH_2O$.

In contrast to the *cis*-$[TcCl_4(L)_2]$ complexes, corresponding trans products, which can be obtained with ligands having 'soft' donor atoms such as PPh_3 or thioxane, are stable against hydrolysis.

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Supporting Information Available: Crystallographic data in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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