$[TcCl_4(H_2O)_2]$ and $[Cl_3(H_2O)_2TcOTc(H_2O)_2Cl_3]$ – two molecular intermediates of the hydrolysis of technetium(IV)†

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Two molecular intermediates of the hydrolysis of technetium tetrachloride, *cis*-$[TcCl_4(H_2O)_2]$ and $[Cl_3(H_2O)_2TcOTc(H_2O)_2Cl_3]$, were isolated and structurally characterised, suggesting that the hydrolytic degradation of technetium(IV) compounds occurs stepwise with the polymeric '$TcO_2\cdots nH_2O$' as a less defined final product.

The oxidation state '+4' of technetium is one of the most stable in the inorganic chemistry of this artificial element. Its coordination chemistry, however, is relatively less explored.[1] This also holds true for the most common starting materials in Tc(IV) chemistry, the $[TcX_6]^{2-}$ complexes anions (X = Cl, Br, I). There are numerous reports of the hydrolysis of such compounds in aqueous media, and the polymeric '$TcO_2\cdots nH_2O$' is discussed as the sole product of these reactions in aqueous media.[1–5]

Indeed, to the best of our knowledge only one crystallographically characterised technetium(IV) aqua complex exists, the $[TcCl_5(H_2O)]^-$ anion, which crystallizes together with an oxonium ion and two molecules of 15-crown-5.[6]

Treatment of technetium(IV) tetrachloride, $TcCl_4$, with water immediately yields insoluble TcO_2, a black-brown, amorphous solid, which contains an undefined amount of water. Thermodynamic model calculations suggest that this hydrolysis proceeds even at pH < 1. Hydrolysed species with mixed oxo, hydroxo and water ligand spheres are formed with increasing pH.[4] Chloride ions were calculated to effect the speciation of Tc(IV) in such solutions through (i) interactions with positively charged hydrolysed Tc(IV) species and (ii) the formation of Tc(IV) chloro complexes.[5] Isolation of such species from aqueous solutions has failed until now. With the stepwise hydrolysis of $TcCl_4$ in moist dioxane, we were now able to isolate two molecular intermediates of this reaction in crystalline form.

$TcCl_4$ (**I**) crystallizes in polymeric chains where the Tc atoms are bridged by chloro ligands giving edge-sharing, distorted octahedra with three distinct Tc–Cl bond lengths. The longest ones (2.49 Å) are associated with the bridging chlorine atoms perpendicular to the chain[7]. The latter weak bonds are readily opened during reactions with donor solvents such as acetonitrile or alkylisocyanides. The formation of $[TcCl_4(solvent)_2]$ complexes was claimed on the basis of spectroscopic data.[4] This has now been confirmed by the isolation of *cis*-$[TcCl_4(CH_3CN)_2]$ (**2**) and determination of its X-ray crystal structure (Fig. 1).‡ The compound is readily formed after dissolution of $TcCl_4$ in dry CH_3CN. It crystallises as yellow plates upon concentration of the obtained yellow solution. The technetium atom is coordinated in a slightly distorted octahedral manner. Tc–N bonds of 2.125(5) Å suggest comparably weak bonds to the CH_3CN ligands, while the Tc–Cl bonds are in the typical range.[8]

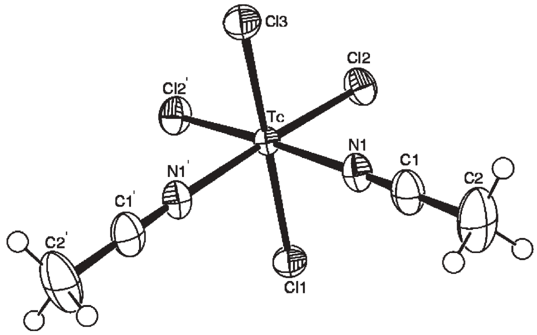
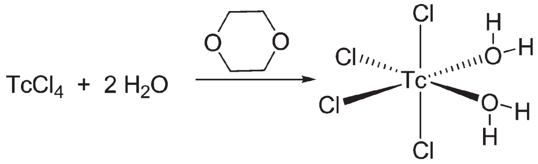


Fig. 1 Structure of **2**. Selected bond lengths (Å) and angles (°): Tc–N1 2.123(5), Tc–Cl1 2.323(2), Tc–Cl2 2.279(2), Tc–Cl3 2.308(2); N1–Tc–N1′ 88.1(3), N1–Tc–Cl2 88.8(1), N1–Tc–Cl2′ 176.8(1), Cl2–Tc–Cl2′ 94.17(9). More bonding parameters and a packing diagram of **2**·CH_3CN are given in Fig. S1 and Table S1 of the ESI†.

The *cis*-arrangement of the CH_3CN ligands in **2** clearly contrasts the bonding situation in the few other structurally characterized $[TcCl_4(L)_2]$ complexes (L = tertiary phosphines or tetrahydrothiophene)[9], which were prepared by standard procedures starting from $[TcCl_6]^{2-}$ and contain the organic ligands in *trans*-positions to each other.



Dissolution of $TcCl_4$ in dioxane does not result in the formation of stable dioxane complexes. The two vacant coordination positions of the metal are occupied by aqua ligands, which are taken from (the carefully dried) solvent or residual traces of water on the glassware. The product, *cis*-$[TcCl_4(H_2O)_2]$ (**3**), can be isolated by concentration of the clear solution as yellow-green blocks.† It is a molecular intermediate of the hydrolysis of $TcCl_4$ and the possibility of isolating this compound in crystalline form is strongly related to the formation of hydrogen bonds to dioxane solvent molecules. They surround the $[TcCl_4(H_2O)_2]$ molecules and, thus, prevent polymerisation. The crystals of **3**·2dioxane are

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† Electronic supplementary information (ESI) available: Tables S1 and S2 and Figures S1–S3. See DOI: 10.1039/b509686c

stable in a dry atmosphere that is saturated with dioxane. Attempts to dry the compound in vacuum, however, result in the collapse of the large green crystals and the formation of brown, oily decomposition products, which finally yield the insoluble $TcO_2\cdots nH_2O$. Our attempts to use **3**·2dioxane as a well defined Tc(IV) precursor with a Tc : O ratio of 1 : 2 for the preparation of solvate-free TcO_2 have failed up to now. This is mainly due to problems maintaining absolutely dry conditions, since we are presently restricted to a standard Schlenck technique during our work with radioactive materials.

The molecular structure of **3** is depicted in Fig. 2a showing two aqua ligands in a *cis* arrangement. The Tc–O bond lengths of 2.096(7) Å are similar to the corresponding value in the $[TcCl_5(H_2O)]^-$ anion.[6] The Tc–Cl bonds *trans* to the water ligands are slightly shortened with respect to those which have Cl^- in *trans* positions. This is explained by the marginal *trans*-labilising influence of aqua ligands. Main distortions of the almost octahedral coordination environment of technetium are due to the fact that the chloro ligands are bent toward the H_2O ones. All hydrogen atoms of the $[TcCl_4(H_2O)_2]$ molecules are involved in hydrogen bonds with molecules of solvate dioxane. This results in an infinite chain along the crystallographic *c* axis and embeds the molecules of **3** into an organic framework, which provides considerable protection against further hydrolysis and immediate polymerisation. Details of the hydrogen bonds are given in Fig. 2b and Table 1. A cell plot and a view showing the direct environment of the $[TcCl_4(H_2O)_2]$ molecules in the solid state structure of **3**·2dioxane are contained in Fig. S2 of the ESI†.

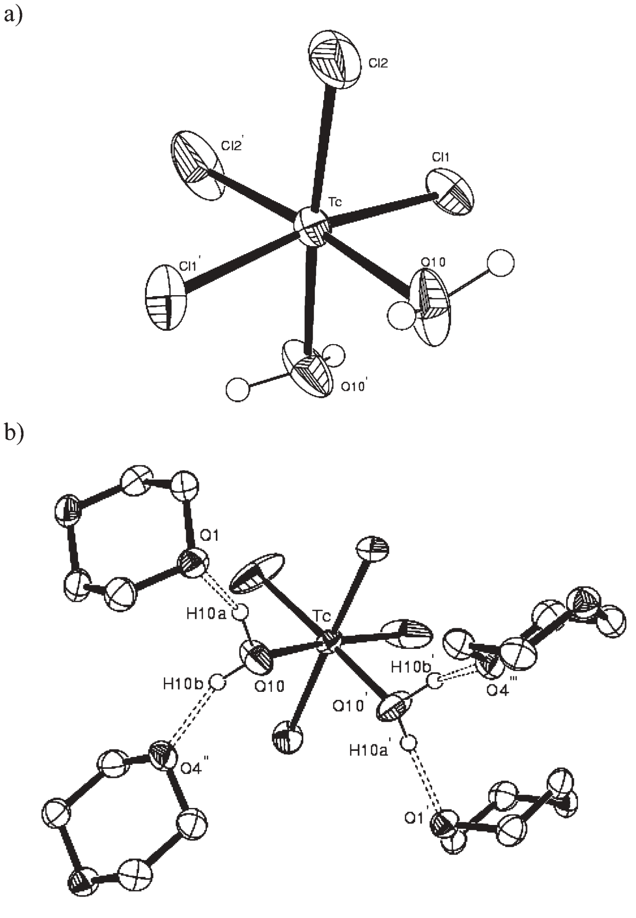
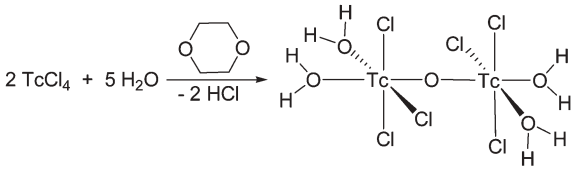


Fig. 2 a) Ellipsoid representation of **3**. Selected bond lengths (Å) and angles (°): Tc–O10 2.096(7), Tc–Cl1 2.331(2), Tc–Cl2 2.283(3), O10–Tc–O10′ 84.9(5), O10–Tc–Cl1 86.5(2), O10–Tc–Cl2 90.2(3) (symmetry transformation: 0.5 − x, −0.5 − y, z); b) Hydrogen bonds between **3** and 4 molecules of dioxane in the solid state structure of **3**·2dioxane. Hydrogen atoms of dioxane are omitted for clarity. For symmetry transformations see Table 1.



Solutions of **3** in dioxane slowly change their colour from pale green to brown. This is a consequence of proceeding hydrolysis with traces of water, and the rate of this conversion increases when the mixture is exposed to air or when $TcCl_4$ is dissolved in freshly distilled, but not dried, dioxane. Concentration of the clear brown solutions results in the formation of golden-brown crystals, which contain $[\{TcCl_3(H_2O)_2\}_2O]$ (**4**) as a dioxane solvate.‡ An additional IR band at 798 cm^{-1} suggests the formation of a Tc–O–Tc bridge. Crystals of **4**·6dioxane are moderately stable in dry air, but rapidly decompose in the presence of moisture or in vacuum. The final decomposition product is amorphous $TcO_2\cdots nH_2O$.

An X-ray study on a single crystal of **4**·6dioxane confirms the composition of **4** as an oxo-bridged dimeric complex. The formation of an oxygen bridge between two Tc(IV) centres is remarkable and without precedent. Fig. 3 illustrates the structure of the molecule. The Tc–O bond lengths of 1.8124(8) Å in the central Tc–O–Tc unit are relatively short and suggest considerable π-bonding involving the donation of electrons from the p_x and p_y orbitals of oxygen to d_π orbitals on the metal ion. A similar bonding situation was observed previously for Tc(V),[10] Tc(III),[11]

Table 1 Hydrogen bonds in **3**·2dioxane

D–H···A	*d* (D–H)	*d* (H···A)	*d* (D···A)	<(DHA)
O10–H10a–O1	0.97	1.75	2.607(7)	146.4
O10–H10b–O4″	0.96	1.76	2.58(1)	140.7

[a] Symmetry transformations used to generate equivalent atoms: (') 0.5 − x, -0.5 − y,z; ('') 0.25 + x,−0.25 − y, −0.25 + z.

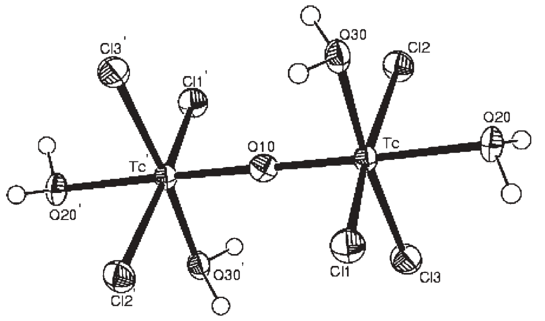


Fig. 3 a) Ellipsoid representation of **4** Selected bond lengths (Å) and angles (°): Tc–O10 1.8124(8), Tc–O20 2.132(3), Tc–O30 2.116(4), Tc–Cl1 2.344(2), Tc–Cl2 2.346(2), Tc–Cl3 2.317(2). O20–Tc–O10 178.67(9), Tc–O–Tc′ 180°. Symmetry transformation: (') 1 − x,−y, 1 − z.

and some mixed-valent complexes, which also contain bridging oxo ligands.[12]

As discussed for compound **3**, the technetium aqua complex **4**·6dioxane also establishes several hydrogen bonds to dioxane solvate molecules. They surround the metal complex and induce some stability against ongoing hydrolysis. Details of the hydrogen bonds and the packing diagram of the compound are contained in Fig. S3 and Table S2 of the ESI†.

$TcCl_4$ has been shown to be an excellent starting material for the synthesis of novel technetium(IV) compounds such as *cis*-$[TcCl_4(CH_3CN)_2]$. The knowledge of the hydrolysis of Tc(IV) compounds gives new impulses to (I) the radiopharmaceutical chemistry of technetium, since many 'classical' Tc radiopharmaceuticals are Tc(IV) compounds, (II) the geochemistry of this element in light of nuclear waste treatment procedures and (III) the fundamental chemistry of the group(VII) elements, since a similar behaviour is also expected for rhenium. The new compounds represent promising precursors for further ligand exchange reactions on the way to new Tc(IV) complexes, but are also very interesting as starting materials for the synthesis of hitherto unknown technetium(III) aqua complexes. The possibility of preparing $[Tc(H_2O)_6]^{3+}$ by electrochemical reduction of appropriate Tc(IV) precursors has been suggested, but the isolation of the product did not succeed starting from $[TcX_6]^{2-}$ complexes (X = Cl, Br).[13] Corresponding experiments are currently being undertaken in our laboratory.

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Notes and references

‡ *Syntheses:* $[TcCl_4(CH_3CN)_2]\cdot CH_3CN$ (**2**): $TcCl_4$ (24 mg, 0.1 mmol) is mixed with 3 ml of dry acetonitrile and stirred at room temperature for 2 h. The volume of the resulting clear yellow solution is reduced in vacuum to about 1 ml and kept overnight at −20 °C. Yellow crystals of $[TcCl_4(CH_3CN)_2]\cdot CH_3CN$ are deposited on the glass walls. More product can be recovered by further removal of the solvent. Yield: almost quantitative. IR: $\nu_{C\equiv N}$ 2315, 2287, ν_{TcCl} 369, 322 cm^{-1}. Elemental analysis (dried sample): Calcd. for $C_4H_6Cl_4N_2Tc$: Tc 30.4%, Found Tc: 29.9%.

$[TcCl_4(H_2O)_2]\cdot 2$ dioxane (**3**): $TcCl_4$ (24 mg, 0.1 mmol) is dissolved in 3 ml of dried dioxane. The mixture is stirred for 3 h at room temperature. The volume of the resulting green solution is reduced in vacuum to about 1 ml. Green crystals of **3** precipitate upon standing overnight at room temperature. Yield 45%. More product can be recovered by further concentration of the mother liquor. This material, however, is contaminated with some brown crystals of **4**. .IR: $\nu_{Tc–Cl}$ 360, 339, $\nu_{Tc–O}$ 436 cm^{-1}, $\rho_{r(water)}$ 675, $\rho_{w(water)}$ 501, $\nu_{(OH,\ H\text{-}bonded)}$ 2870 cm^{-1}. Technetium analysis did not give satisfying results due to proceeding hydrolysis of the compound.

$[\{TcCl_3(H_2O)_2\}_2O]\cdot 6$ dioxane (**4**): $TcCl_4$ (24 mg, 0.1 mmol) is dissolved in 3 ml of dioxane, which has not been dried. The mixture is stirred for 3 h at room temperature. The volume of the resulting dark green solution is reduced in vacuum to about 1 ml. Golden-brown crystals of **3** precipitate upon standing overnight at room temperature. Yield 65%. Alternatively, dioxane solutions of **3** can be exposed to air. This results is a change of the colour *via* dark green to brown and single crystals of **4** can be recovered upon concentration. IR: $\nu_{as(Tc–O–Tc)}$ 798, $\nu_{Tc–Cl}$ 375, 351, $\nu_{Tc–O(water)}$ 472 cm^{-1}, $\rho_{r(water)}$ 575, $\rho_{w(water)}$ 473, $\nu_{(OH,\ H\text{-}bonded)}$ 2854 cm^{-1}. Technetium analysis did not give satisfying results due to proceeding hydrolysis of the isolated compound.

Crystal structure determinations: STOE IPDS, Mo Kα radiation, solution and refinement: SHELXS and SHELXL.[14]

2·CH₃CN: $C_6H_9Cl_4N_3Tc$, M = 362.96, orthorhombic, *Pnma*, a = 10.325(5), b = 13.531(5), c = 9.720(5) Å, V = 1358(1) Å^3, Z = 4, D_{calc} = 1.775 g cm^{-3}, θ 3.25–26.80°, T = 193 K, 4069 reflections, μ = 1.775 mm^{-1} (no absorption correction), 69 parameters, $R1$ = 0.0460, w$R2$ = 0.0877, GoF = 0.921. The solvent acetonitrile is disordered near a centre of symmetry and was refined isotropically. CCDC reference number: 278683.

3·2dioxane: $C_8H_{20}Cl_4O_6Tc$, M = 452.04, orthorhombic, *Fdd*2, a = 18.495(8), b = 25.730(5), c = 7.023(5) Å, V = 3342(3) Å^3, Z = 8, D_{calc} = 1.797 g cm^{-1}, θ 2.68–26.38°, T = 173 K, 1957 reflections, μ = 1.516 mm^{-1} (absorption correction: integration, T_{min} = 0.7953, T_{max} = 0.8386), 88 parameters, $R1$ = 0.0282, w$R2$ = 0.0923, GoF = 1.102. CCDC reference number: 278684.

4·6dioxane: $C_{24}H_{56}Cl_6O_{16}Tc_2$, M = 1025.38, triclinic, $P\bar{1}$, a = 10.054(5), b = 10.138(5), c = 10.519(5) Å, α = 98.82(1), β = 102.26(1)°, γ = 91.99(1), V = 1032.8(9) Å^3, Z = 1, D_{calc} = 1.649 g cm^{-1}, θ 2.55–29.21°, T = 193 K, 9898 reflections, μ = 1.112 mm^{-1} (no absorption correction), 223 parameters, R1 = 0.0401, w$R2$ = 0.0570, GoF = 0.588. CCDC reference number: 278685. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b509686c

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