

Water-Soluble Organometallic Complexes of Tantalum: Can Alkyl and Aqua Ligands Coexist in Its Coordination Sphere?

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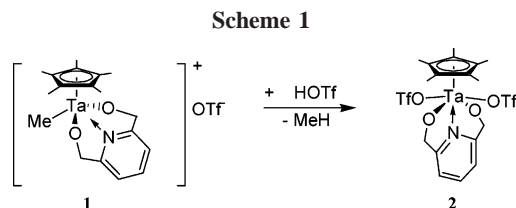
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Summary: The complexes $[\text{Cp}^*\text{TaMe}(\text{OCH}_2)_2\text{py}(\text{H}_2\text{O})]\text{OTf}$ (**3**), $[\text{Cp}^*\text{Ta}(\text{OH})(\text{OCH}_2)_2\text{py}(\text{H}_2\text{O})]\text{OTf}$ (**4**), and $[\text{Cp}^*\text{Ta}(\text{OCH}_2)_2\text{py}(\text{H}_2\text{O})_2]\text{OTf}_2$ (**5**) are described as the first examples of water-soluble organometallic derivatives of tantalum.

Water-soluble organometallic complexes have been of increasing interest in recent years, due to the many advantages an aqueous medium presents to stoichiometric and catalytic reactions.¹ Water is a readily available solvent and is environmentally benign. This, along with its distinct physical properties, makes it an ideal solvent for numerous catalytic processes. Furthermore, the development of water-soluble metal complexes is also a primary requirement in biomedicine.²

To achieve the synthesis of water-soluble organometallic derivatives, several strategies have been developed. The most widely used is the design of water-soluble ligands that when incorporated into the coordination sphere of the metal impart water solubility to the complexes.³ However, going back to classical coordination chemistry, many complexes containing aqua and hydroxo ligands in the coordination sphere of the metal are water soluble because of their ionic charge and their hydrogen-bonding ability.⁴ Furthermore, as found in biological systems, water is also interesting because it can participate in structure-directing intermolecular interactions, leading to supramolecular assemblies in these systems.⁵

An important drawback of this approach in early-transition-metal chemistry is the easy hydrolysis of the M–C bonds. Moreover, the M–OR bonds of ancillary ligands such as alkoxides or aryloxides are also easily hydrolyzed. In this regard,



the hydrolysis of metal alkoxides is a ubiquitous reaction, and it is the basis for the sol–gel route of metal oxide synthesis.⁶

Herein, we now report the successful synthesis and solid-state structural characterization of several organometallic complexes of tantalum which are, to our knowledge, the first water-soluble organometallic derivatives of tantalum.

The tantalum complex $[\text{Cp}^*\text{TaMe}(\text{OCH}_2)_2\text{py}]\text{OTf}$ (**1**)⁷ reacts with triflic acid in a 1:1 molar ratio to yield the corresponding bis(triflate) compound $[\text{Cp}^*\text{Ta}(\text{OTf})_2(\text{OCH}_2)_2\text{py}]$ (**2**)⁸ (Scheme 1). Complex **2** is soluble in toluene or THF and less soluble in pentane. It has been characterized by the normal spectroscopic and analytical techniques. The NMR data are consistent with a trans disposition of the triflate ligands and the coordination of the alkoxide group as a “pincer” ligand, analogous to the conformation reported for $[\text{Cp}^*\text{TaCl}_2(\text{OCH}_2)_2\text{py}]$.⁷

This proposal has been confirmed by an X-ray diffraction study. Figure 1 shows the molecular diagram of **2**.

Moreover, complex **1** reacts with water, to yield the corresponding water-containing complex $[\text{Cp}^*\text{TaMe}(\text{OCH}_2)_2\text{py}(\text{H}_2\text{O})]\text{OTf}$ (**3**)⁹ (Scheme 2). Complex **3** is air-stable in the solid state, soluble in dichloromethane, partially soluble in water, and insoluble in toluene or pentane. It has been characterized by the normal spectroscopic and analytical techniques as well as by X-ray diffraction methods.

The ¹H NMR of **3** in D₂O shows singlet signals at –0.49 and 1.91 ppm corresponding to the methyl group bonded to the tantalum center and to the Cp* ligand, respectively. In addition, the methylene moieties give rise to two doublet signals at 5.61

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(8) Synthesis of **2**: to a solution of $[\text{Cp}^*\text{TaMe}(\text{OCH}_2)_2\text{py}]\text{OTf}$ (**1**; 0.250 g, 0.40 mmol) in 6 mL of CH₂Cl₂ was slowly added triflic acid (0.038 mL), and the mixture was stirred for 1 h at room temperature. The solvent was removed under vacuum and the residue washed with 5 mL of pentane to yield 0.230 g (75%) of complex **2**. ¹H NMR (CDCl₃, room temperature, 200 MHz): δ 2.34 (s, 15 H, Cp*), 6.32, (s, 4 H, CH₂), 7.38 (d, ³J_{H–H} = 8.78 Hz, 2 H, Ar), 7.96 (t, ³J_{H–H} = 8.78 Hz, 1 H, Ar). ¹³C{¹H} NMR (CDCl₃): δ 11.6 (s, Cp*), 83.0 (s, CH₂), 117.9 (s, Ar), 129.0 (s, Cp*), 142.4 (s, Ar), 166.4 (s, Ar_{ipso}). ¹⁹F{¹H} NMR (CDCl₃): δ –77.59 (s, CF₃SO₃). Anal. Calcd for C₁₉H₂₂O₈F₆S₂N₂Ta: C, 30.36; H, 2.95; N, 1.86. Found: C, 30.38; H, 3.11; N, 2.16.

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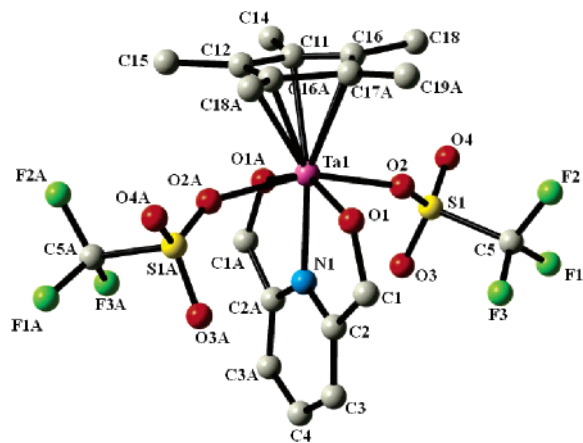


Figure 1. Molecular diagram of $[\text{Cp}^*\text{Ta}(\text{OTf})_2(\text{OCH}_2)_2\text{py}]$ (**2**). Some important bond distances (\AA) and angles (deg): $\text{Ta}(1)-\text{O}(1) = 1.930(4)$, $\text{Ta}(1)-\text{O}(1)^a = 1.930(4)$, $\text{Ta}(1)-\text{O}(2) = 2.129(4)$, $\text{Ta}(1)-\text{N}(1) = 2.164(6)$, $\text{O}(1)-\text{C}(4) = 1.416(8)$; $\text{O}(1)-\text{Ta}(1)-\text{O}(1)^a = 148.2(3)$, $\text{O}(2)-\text{Ta}(1)-\text{O}(2)^a = 158.6(2)$, $\text{C}(4)-\text{O}(1)-\text{Ta}(1) = 125.7(4)$. Symmetry transformation used to generate equivalent atoms: (a) $-x + 1, y, -z + 3/2$.

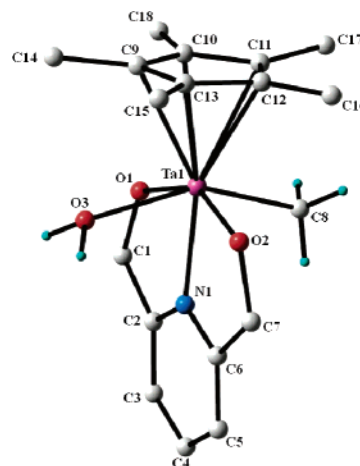
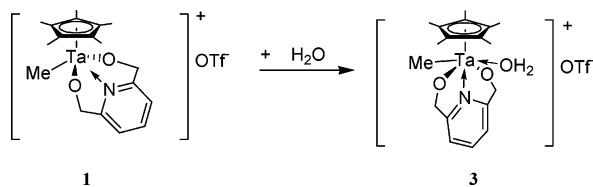
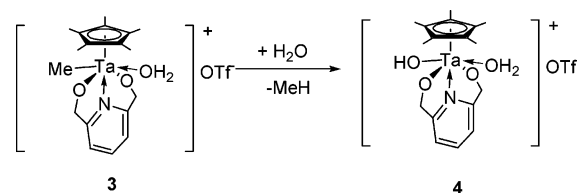


Figure 2. Molecular diagram of $[\text{Cp}^*\text{TaMe}(\text{OCH}_2)_2\text{py}(\text{H}_2\text{O})]\text{OTf}$ (**3**). Some important bond distances (\AA) and angles (deg): $\text{Ta}(1)-\text{O}(1) = 1.939(4)$, $\text{Ta}(1)-\text{O}(2) = 1.949(4)$, $\text{Ta}(1)-\text{O}(3) = 2.274(4)$, $\text{Ta}(1)-\text{N}(1) = 2.189(4)$, $\text{Ta}(1)-\text{C}(8) = 2.196(5)$; $\text{O}(1)-\text{Ta}(1)-\text{O}(2) = 147.1(2)$, $\text{C}(8)-\text{Ta}(1)-\text{O}(3) = 153.8(2)$, $\text{C}(1)-\text{O}(1)-\text{Ta}(1) = 125.5(3)$.

Scheme 2



Scheme 3



and 5.79 ppm, while the aromatic protons appear as multiplet signals at 7.34 and 7.88 ppm. The same pattern is observed when the ^1H NMR spectrum is recorded in CDCl_3 , and in addition, a broad resonance corresponding to the aqua ligand appears at 2.51 ppm. ^1H NMR spectra in both D_2O and in CDCl_3 are in agreement with the coordination of the water molecule in a position trans to the methyl group. This proposal has been confirmed by an X-ray diffraction study. Figure 2 shows the molecular diagram of **3**.

The coordination around the metal is best described as a pseudo-octahedral geometry. The tantalum atom is bonded to the cyclopentadienyl ring in an η^5 mode. On the other hand, the alkoxide ligand is bonded to the metal in a "pincer" fashion, with the nitrogen of the pyridinic moiety in a position trans to the Cp^* group. In addition, the methyl and aqua ligands are in the equatorial plane, in positions trans to each other. The $\text{Ta}(1)-\text{O}(1)$ and $\text{Ta}(1)-\text{O}(2)$ bond distances, 1.939(4) and 1.949(4) \AA , respectively, compare well with those found in other tantalum complexes containing this alkoxide ligand and are within the normal range for tantalum alkoxide complexes.¹⁰ The

$\text{Ta}-\text{N}$ bond length (2.189(4) \AA) is rather short and is comparable to that found in anionic nitrogen ligands.¹¹ On the other hand, the $\text{Ta}(1)-\text{C}(8)$ bond distance, 2.196(5) \AA , is short but is within the expected range for tantalum alkyl complexes.¹² The $\text{Ta}(1)-\text{O}(3)$ bond length, 2.274(4) \AA , is normal for tantalum aqua complexes.¹³ In the crystal two cations and two anions are packed together via hydrogen bonds involving the coordinated water molecules and the triflate ions.

It is worth pointing out that, to the best of our knowledge, this is the first example of a complex of tantalum in which both water and methyl groups are simultaneously bonded to the same metal center. Thus, the record is completely silent regarding any report of isolable or spectroscopically observable tantalum alkyl aqua complexes. The inertness of the $\text{Ta}-\text{C}$ σ bond in our complex toward hydrolysis is an unusual feature for early-transition-metal alkyl complexes. The only example we have found in which a protic ligand and a methyl group are bonded to the same tantalum center is the bis(pentamethylcyclopentadienyl)tantalum derivative $[\text{Cp}^*_2\text{TaMe}(\text{OH})][\text{B}(\text{OH})(\text{C}_6\text{F}_5)_3]$.¹⁴

In order to determine to what extent the nature of the anion affects the properties of the complex, we have tried to replace the OTf^- group by BPh_4^- . Compound **3** reacts at room temperature in CH_2Cl_2 with NaBPh_4 to yield a mixture of unidentified complexes, none of which keeps the $\text{Ta}-\text{Me}$ bond.

(9) Synthesis of **3**: to a solution of complex **1** (0.124 g, 0.20 mmol) in THF was added an excess of water, and this mixture was left at room temperature for 12 h. The solvent was removed under vacuum and the residue washed with 5 mL of pentane to yield complex **3** (0.099 g, 77%). Colorless crystals of **3** can be obtained by slow diffusion of pentane into a THF solution. ^1H NMR (CDCl_3 , room temperature, 200 MHz): δ -0.41 (s, 3 H, $\text{Ta}-\text{Me}$), 2.08 (s, 15 H, Cp^*), 2.51 (br, 2 H, H_2O), 5.82 (d, $^2J_{\text{H}-\text{H}} = 18.33$ Hz, 2 H, CH_2), 6.09 (d, $^2J_{\text{H}-\text{H}} = 18.33$ Hz, 2 H, CH_2), 7.33 (d, $^3J_{\text{H}-\text{H}} = 8.06$ Hz, 2 H, Ar), 7.90 (t, $^3J_{\text{H}-\text{H}} = 8.06$ Hz, 1 H, Ar). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 11.4 (s, Cp^*), 37.5 (s, Me), 81.0 (s, CH_2), 118.0 (s, Ar), 123.2 (s, Cp^*), 140.7 (s, Ar), 165.1 (s, Ar_{ipso}). $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3): δ -78.66 (s, CF_3SO_3). ^1H NMR (D_2O , room temperature, 200 MHz): δ -0.49 (s, 3 H, $\text{Ta}-\text{Me}$), 1.91 (s, 15 H, Cp^*), 5.61 (d, $^2J_{\text{H}-\text{H}} = 17.96$ Hz, 2 H, CH_2), 5.79 (d, $^2J_{\text{H}-\text{H}} = 17.96$ Hz, 2 H, CH_2), 7.34 (m, 2 H, Ar), 7.88 (m, 1 H, Ar). $^{19}\text{F}\{^1\text{H}\}$ NMR (D_2O): δ -79.39 (s, CF_3SO_3). Anal. Calcd for $\text{C}_{19}\text{H}_{27}\text{O}_6\text{F}_3\text{SNTa}$: C, 35.91; H, 4.28; N, 2.20. Found: C, 35.62; H, 4.29; N, 2.15.

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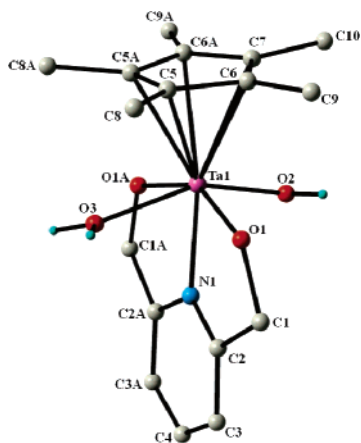


Figure 3. Molecular diagram of $[\text{Cp}^*\text{Ta}(\text{OH})(\text{OCH}_2)_2\text{py}(\text{H}_2\text{O})]\text{OTf}$ (**4**). Some important bond distances (Å) and angles (deg): $\text{Ta}(1)\text{--O}(1) = 1.96(2)$, $\text{Ta}(1)\text{--O}(1)^b = 1.96(2)$, $\text{Ta}(1)\text{--O}(3) = 2.17(2)$, $\text{Ta}(1)\text{--N}(1) = 2.14(2)$, $\text{Ta}(1)\text{--O}(2) = 1.95(1)$; $\text{O}(1)^b\text{--Ta}(1)\text{--O}(1) = 148.4(8)$, $\text{O}(2)\text{--Ta}(1)\text{--O}(3) = 154.9(7)$, $\text{C}(1)\text{--O}(1)\text{--Ta}(1) = 124.5(15)$. Symmetry transformations used to generate equivalent atoms: (b) $x, -y + 1/2, z$.

The Ta–Me bond in complex **3** hydrolyzes slowly in H_2O at room temperature. At 90°C the hydrolysis process becomes faster, yielding the corresponding hydroxo derivative **4**¹⁵ (Scheme 3).

Complex **4** is air-stable in the solid state, soluble in dichloromethane and in water, and insoluble in toluene or pentane. It has been characterized by NMR spectroscopy. The molecular structure of the complex has been confirmed by an X-ray diffraction study. Figure 3 shows the molecular diagram of the cationic moiety in **4**.

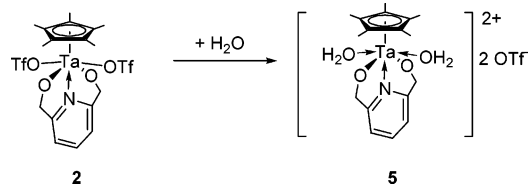
The geometry around tantalum is, as in complexes **2** and **3**, pseudo-octahedral. The hydroxo group and the water molecule are in the equatorial plane, trans to each other. The intramolecular Ta–N, Ta–C, and Ta–O bond lengths are very similar to those found in complex **3**.

Complex **4** is interesting, because there are few structures available for organometallic hydroxotantalum complexes and none of them are reported to be water soluble.¹⁶ In addition, hydroxo complexes of transition metals have been postulated

(15) Synthesis of **4**: a suspension of complex **3** (0.103 g, 0.16 mmol) in water was heated to 90°C for 30 min. The solvent was removed under vacuum and the residue washed with 5 mL of Et_2O to yield a white compound that was characterized as **4** (0.084 g, 81%). Colorless crystals of $\mathbf{4}\cdot\text{H}_2\text{O}$ can be obtained by slow cooling of a saturated solution of **4** in H_2O . pH (room temperature, 7.5 mM solution): 4.46. ^1H NMR (D_2O , room temperature, 200 MHz): δ 1.96 (s, 15 H, Cp*), 5.74 (s, 4 H, CH_2), 7.36 (d, $^3J_{\text{H--H}} = 7.5$ Hz, 2 H, Ar), 7.94 (t, $^3J_{\text{H--H}} = 7.5$ Hz, 1 H, Ar). ^{19}F NMR (D_2O): δ -79.4 (OTf). $^{13}\text{C}\{^1\text{H}\}$ NMR (D_2O): δ 9.9 (s, Cp*), 79.3 (s, CH_2), 118.1 (s, Ar), 124.8 (s, Cp*), 141.4 (s, Ar), 162.6 (s, Ar_{ipso}). ^1H NMR (CDCl_3 , room temperature, 200 MHz): δ 2.04 (s, 15 H, Cp*), 2.9 (br, 2 H, H_2O), 4.70 (br, 1 H, OH), 6.01 (br, 4 H, CH_2), 7.26 (d, $^3J_{\text{H--H}} = 7.7$ Hz, 2 H, Ar), 7.90 (t, $^3J_{\text{H--H}} = 7.7$ Hz, 1 H, Ar). $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3): δ -78.38 (s, CF_3SO_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 11.3 (s, Cp*), 80.5 (s, CH_2), 117.9 (s, Ar), 125.3 (s, Cp*), 141.2 (s, Ar). Anal. Calcd for $\text{C}_{18}\text{H}_{27}\text{O}_8\text{F}_3\text{SNTa}$: C, 32.98; H, 4.15; N, 2.13; S, 4.89. Found: C, 33.04; H, 3.88; N, 2.21; S, 5.00.

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Scheme 4



as critical intermediates in a number of catalytic reactions involving water as a substrate.¹⁷

Moreover, complex **2** reacts with water to yield the corresponding cationic complex $[\text{Cp}^*\text{Ta}(\text{OCH}_2)_2\text{py}(\text{H}_2\text{O})_2]\text{OTf}_2$ (**5**)¹⁸ (Scheme 4). In this way, water replaces the triflate group from the coordination sphere of the tantalum center, yielding the corresponding dicationic tantalum derivative. Complex **5** is air stable, soluble in water, less soluble in dichloromethane, and insoluble in toluene or THF. The ^1H NMR spectrum in D_2O shows singlet signals at 2.00 and 5.93 ppm, assigned to the Cp* ligand and to the methylene protons of the dialkoxide ligand. The aromatic protons appear as multiplet signals at 7.38 and 7.92 ppm. The spectrum is in agreement with the coordination of the two water molecules to the tantalum center in positions trans to each other.

In water solution complex **5** is acidic enough to propose that under these conditions an aqua ligand becomes a hydroxo group. Moreover, complex **4** can be protonated with HOTf in H_2O in a 1:1 molar ratio, to yield **5**. In addition, the ^1H NMR of an equimolar mixture of complexes **4** and **5** in D_2O shows that they are in rapid interchange.

In conclusion, we report here the synthesis and characterization of the first water-soluble organotantalum complexes. We have shown that the pincer tantalum alkoxide moiety exhibits a remarkable stability toward hydrolysis and allows the synthesis of several aqua and hydroxo compounds that can be considered as soluble models of hydrated tantalum oxide and could be useful starting materials for the synthesis of new water-soluble organometallic tantalum derivatives.

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Supporting Information Available: Text, tables, figures, and CIF files giving full experimental data for the crystallographic studies of compounds **2–4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(18) Synthesis of **5**: to a solution of $[\text{Cp}^*\text{Ta}(\text{OTf})_2(\text{OCH}_2)_2\text{py}]$ (0.323 g, 0.43 mmol) in 6 mL of toluene was added an excess of water (0.5 mL), and the mixture was stirred for 48 h at room temperature. The solvent was filtered off and the residue washed with 5 mL of Et_2O and dried under vacuum to yield 0.284 g (84 %) of complex **5**. pH (room temperature, 7.8 mM solution): 1.81. ^1H NMR (D_2O , room temperature, 200 MHz): δ 2.00 (s, 15 H, Cp*), 5.93 (s, 4 H, CH_2), 7.38 (d, $^3J_{\text{H--H}} = 7.70$ Hz, 2 H, Ar), 7.92 (t, $^3J_{\text{H--H}} = 7.70$ Hz, 1 H, Ar). ^{19}F NMR (D_2O): δ -79.4 (OTf). $^{13}\text{C}\{^1\text{H}\}$ NMR (D_2O): δ 10.1 (s, Cp*), 80.8 (s, CH_2), 118.5 (s, Ar), 126.3 (s, Cp*), 142.1 (s, Ar), 162.4 (s, Ar_{ipso}). Anal. Calcd for $\text{C}_{19}\text{H}_{26}\text{O}_{10}\text{F}_6\text{S}_2\text{NTa}$: C, 28.98; H, 3.32; N, 1.77; S, 8.14. Found: C, 29.08; H, 3.35; N, 1.85; S, 7.74.