

The Ru(II)-supported heptatungstates [HXW₇O₂₈Ru(dmsO)₃]⁶⁻ (X = P, As)[†]

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Received (in Cambridge, UK) 7th April 2005, Accepted 13th June 2005

First published as an Advance Article on the web 6th July 2005

DOI: 10.1039/b504903m

The ruthenium(II)-supported heteropolyanions [HXW₇O₂₈Ru(dmsO)₃]⁶⁻ (X = P, **1**; As, **2**) are composed of a Ru(dmsO)₃ group attached to an unprecedented heptatungstate fragment *via* two Ru–O–W bonds and one Ru–O–X bond, which represents a fundamentally novel mode of Ru-coordination to a polyoxoanion framework. Multinuclear ¹⁸³W, ³¹P, ¹³C, and ¹H NMR studies indicate high stability of **1** and **2** in solution.

Polyoxometalates (POMs) constitute a large and distinctive class of molecular inorganic compounds with fascinating structural variety combined with remarkable chemical properties resulting in their widespread potential in different fields including catalysis, materials science and medicine.^{1–6} Over the past few years research on POMs has greatly expanded and strong efforts have been devoted to prepare functionalized POMs *via* incorporation or coordination of organometallic or organic moieties to produce novel selective and highly efficient catalytic systems.^{7,8}

Ruthenium-substituted POMs are of particular interest in this field, due to the redox-active nature of ruthenium.⁹ Especially the group of Neumann has engaged in a number of studies on the catalytic properties of ruthenium-containing polyanions.¹⁰ To date it is well established that ruthenium-POMs exhibit high reactivity and selectivity in the catalytic oxidation of a variety of organic substrates by O₂ and H₂O₂.¹¹ The dimethyl sulfoxide (dmsO) complex *cis*-Ru(dmsO)₄Cl₂ has become a popular ruthenium(II) precursor for the synthesis of ruthenium-substituted polyanions.¹² However, the number of structurally characterized ruthenium-containing polyoxomolybdates¹³ and polyoxotungstates¹⁴ is very small. Very recently our group discovered the novel Ru^{II}(dmsO)₃-supported polyanions [HW₉O₃₃Ru₂(dmsO)₆]⁷⁻ and [Ru(dmsO)₃(H₂O)XW₁₁O₃₉]⁶⁻ (X = Ge, Si) with completely unprecedented structures.¹⁵ The search for novel polyanion structures containing ruthenium is a hot area of research, as only a detailed structural understanding of the catalyst or pre-catalyst allows for rational catalytic investigations including mechanistic work.

Herein we present two novel and isostructural Ru^{II}(dmsO)₃-supported heteropolyanions and their solution and solid state characterization.

Single crystal X-ray analysis on Cs₄Na₂[HPW₇O₂₈Ru(dmsO)₃]·12H₂O (**1a**) and Cs₂Na₄[HAsW₇O₂₈Ru(dmsO)₃]·8H₂O (**2a**) revealed the novel polyanions [HXW₇O₂₈Ru(dmsO)₃]⁶⁻ (X = P, **1**; As, **2**), which are composed of a Ru(dmsO)₃ group attached to an unprecedented heptatungstate fragment resulting in an unusually open assembly with C_s symmetry (Fig. 1).¹⁶ Interestingly, the Ru(dmsO)₃ unit is coordinated *via* two Ru–O–W bonds and one Ru–O–X bond to the polyanion backbone of **1** and **2**. Such bonding of an (organo)Ru fragment involving actively also the hetero group of the polyanion has never been observed before. The inner coordination sphere of ruthenium is completed by the sulfur atoms of three terminal dmsO ligands, resulting in a trigonal antiprismatic coordination geometry (I: Ru–O, 2.072–2.080(7) Å; Ru–S, 2.226–2.231(3) Å). The (XW₇O₂₈) units in **1** (X = P) and **2** (X = As) are composed of one edge-shared W₃O₁₃ triad to which a half-ring of four edge-shared WO₆ octahedra is connected *via* corners and this assembly is stabilized by the central XO₄ group. As a result, the three tungsten centers of the W₃O₁₃ triad have one terminal oxo ligand whereas the remaining four tungsten atoms have two, *cis*-related terminal oxo groups. Therefore, polyanions **1** and **2** do not violate the Lipscomb principle and the heptatungstate fragment adds a novel architectural building block to the rich class of polyoxometalates.

Polyanions **1** and **2** also represent the first structurally characterized tungstophosphate/arsenate assemblies to which an organo-ruthenium fragment has been grafted. Two Ru(dmsO)-tungstophosphates (Bonchio's [Ru^{II}(dmsO)PW₁₁O₃₉]⁵⁻ and Nomiya's [Ru^{II}(dmsO)₂(P₂W₁₇O₆₁)₂]¹⁸⁻) have been postulated, but both species could only be characterized in solution by multinuclear NMR spectroscopy and especially the structure of the latter remains elusive.^{17,18}

Synthesis of **1** can be accomplished by three completely different one-pot procedures, with and without using polyanion precursors.¹⁹ This observation reveals that **1** forms easily and at the same time suggests that it is very stable. The simplest synthesis method for **1** involves reaction of the different elements (*cis*-Ru(dmsO)₄Cl₂, Na₂WO₄ and NaH₂PO₄) in appropriate molar ratios. Secondly, the title polyanion **1** can also be prepared by reacting *cis*-Ru(dmsO)₄Cl₂ with the trilacunary Keggin precursor [A-PW₉O₃₄]⁹⁻ and thirdly, by reacting *cis*-Ru(dmsO)₄Cl₂ with the 'non-lacunary' pentatungstodiphosphate [P₂W₅O₂₃]⁶⁻. To our knowledge there is no precedent of such a phenomenon in polyanion chemistry. Synthesis of **2** was accomplished by reaction of *cis*-Ru(dmsO)₄Cl₂ with the trilacunary Keggin precursor [A-AsW₉O₃₄]^{9–20}

Nevertheless, our results also show that *cis*-Ru(dmsO)₄Cl₂ is essential for the formation of **1** and **2**. Three of the originally four

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† Electronic supplementary information (ESI) available: solution NMR spectra of **1a** (³¹P, ¹³C, ¹H) and **2a** (¹⁸³W, ¹³C, ¹H). See <http://dx.doi.org/10.1039/b504903m>

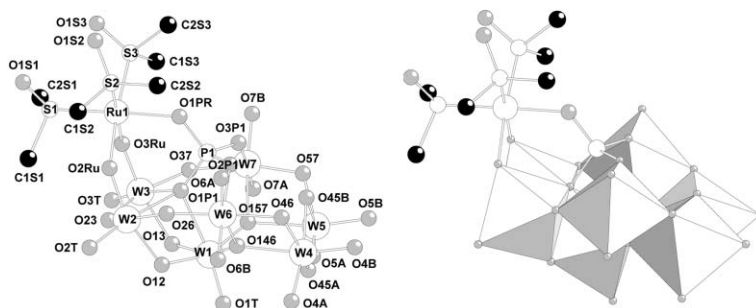


Fig. 1 Ball and stick (left) and polyhedral (right) representations of $[\text{HPW}_7\text{O}_{28}\text{Ru}(\text{dmsO})_3]^{6-}$ (**1**) showing the labeling scheme. This figure is also representative for $[\text{HAsW}_7\text{O}_{28}\text{Ru}(\text{dmsO})_3]^{6-}$ (**2**).

dmsO ligands appear to be rather strongly bound to the Ru(II) center, as they remain attached even after extended heating (*e.g.* 3 h reflux).¹⁹ This observation is in complete agreement with our previous studies, which always (independent of the binding mode of Ru to the polyanion backbone) resulted in products with three dmsO ligands bound to ruthenium.¹⁵

Bond valence sum (BVS) calculations for **1** suggest that the μ_2 -oxo group O45B bridging tungsten centers W4 and W5 (Fig. 1) is monoprotonated, indicating that the charge of the polyanion must be -6 .²¹ The same observation is true for **2**.

We also examined the solution properties of **1** and **2** by multinuclear NMR (D_2O , 20 °C). Tungsten-183 NMR of **1** resulted in four signals at -87.2 , -103.3 , -171.6 and -172.2 ppm, respectively, with intensity ratios of 2:2:2:1 (Fig. 2). This is in complete agreement with the solid state structure of **1**, which indicates the presence of four distinct types of tungsten nuclei.

These results are supported by a singlet at 1.1 ppm in ^{31}P NMR. In ^{13}C -NMR we observed two singlets at 44.0 and 44.1 ppm with an intensity ratio of 2:1. Finally, ^1H -NMR showed three singlets at 3.21, 3.25 and 3.34 ppm, respectively, with intensity ratios of 1:1:1. The three ^1H signals are expected and indicate two distinct types of dmsO ligands (two of the three dmsO are symmetry-related) and three distinct types of methyl groups (two of each kind) in **1**. Also ^{13}C NMR is consistent with the structure of **1**, but the chemical shift differences are so small here that only two types of carbon atoms are resolved. The methyl hydrogens in **1** are expected to be more sensitive to the polyanion symmetry than the methyl carbons, which reflect predominantly the local environment around the Ru-center. Most likely all three dmsO ligands in **1** are hindered from rotation around the Ru-S bond due to steric constraints. As expected, the solution NMR results for **2** are very

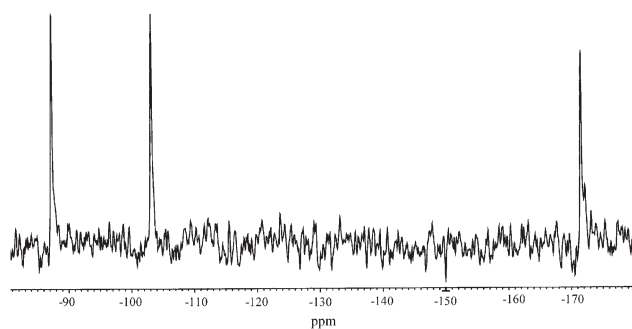


Fig. 2 Room temperature ^{183}W NMR spectrum of $[\text{HPW}_7\text{O}_{28}\text{Ru}(\text{dmsO})_3]^{6-}$ (**1**) in D_2O .

similar to those of **1** and are therefore also fully consistent with the solid state polyanion structure (see ESI†).²²

In conclusion, we have synthesized the novel ruthenium(II)-supported tungstophosphate **1** and the isostructural tungstoarsenate **2**. Interestingly, **1** could be synthesized *via* three completely different synthetic procedures. Polyanions **1** and **2** contain an unprecedented heptatungstate fragment and a novel binding mode of the $\text{Ru}(\text{dmsO})_3$ unit. Due to the open structure of **1** and **2** with its highly accessible organo-ruthenium unit we decided to perform oxidation catalysis, electrochemistry and electrocatalysis studies. All this work is currently in progress and the results will be reported in due time.

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- 16 Crystal data: $\text{Cs}_4\text{Na}_2[\text{HPW}_7\text{O}_{28}\text{Ru}(\text{dmsO})_3]\cdot 12\text{H}_2\text{O}$ (**1a**): $\text{C}_6\text{Cs}_4\text{H}_{43}\text{Na}_2\text{O}_{43}\text{PRuS}_3\text{W}_7$, $M = 2896.4$, monoclinic, $P2_1/n$, $a = 11.8045(10)$, $b = 14.1144(12)$, $c = 30.313(3)$ Å, $\beta = 97.363(4)^\circ$, $V = 5009.0(7)$ Å³, $T = 100$ K, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 19.25$ mm⁻¹, 198710 reflections collected, 12470 unique ($R(\text{int}) = 0.041$), $RI = 0.038$, $wR2 = 0.107$ ($I > (2\sigma(I))$). Crystal data: $\text{Cs}_2\text{Na}_4[\text{HAsW}_7\text{O}_{28}\text{Ru}(\text{dmsO})_3]\cdot 8\text{H}_2\text{O}$ (**2a**): $\text{AsC}_6\text{Cs}_2\text{H}_{35}\text{Na}_4\text{O}_{39}\text{RuS}_3\text{W}_7$, $M = 2648.5$, monoclinic, $P2_1/c$, $a = 14.8022(6)$, $b = 23.4210(10)$, $c = 16.4215(7)$ Å, $\beta = 92.0370(10)^\circ$, $V = 5689.4(4)$ Å³, $T = 298$ K, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 16.01$ mm⁻¹, 55622 reflections collected, 19788 unique ($R(\text{int}) = 0.043$), $RI = 0.066$, $wR2 = 0.196$ ($I > (2\sigma(I))$). We could identify most of the Cs⁺ and Na⁺ counter ions, but no hydrogen atoms by XRD. However, the chemical composition of **1a** and **2a** was confirmed by elemental analysis. CCDC 26781& 26782. See <http://dx.doi.org/10.1039/b504903m> for crystallographic data in CIF or other electronic format.
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- 19 *Procedure 1*: The following reagents were dissolved in 20 mL of pure water with stirring in this order: 0.3 g (0.62 mmol) of *cis*-Ru(dmsO)₄Cl₂, 1.0 g (3.0 mmol) of Na₂WO₄·2H₂O, and 0.06 g (0.44 mmol) of NaH₂PO₄·H₂O. This solution was refluxed for 3 h and then cooled to room temperature. Addition of 1.5 mL of 1.0 M CsCl solution to the orange filtrate and slow evaporation at room temperature led to 0.5 g (yield 40%, based on W) of an orange crystalline product after about two weeks. *Procedure 2*: A 0.25 g (0.52 mmol) sample of *cis*-Ru(dmsO)₄Cl₂ was dissolved in 20 mL sodium acetate buffer (0.5 M, pH 6.5) followed by addition of 0.5 g (0.18 mmol) of Na₈H[A-PW₉O₃₄]·24H₂O. This solution was heated to 50 °C for 1 h and then cooled to room temperature. The solution was filtered and then 0.5 mL of 1.0 M CsCl solution was added. This solution was allowed to evaporate in an open beaker at room temperature. An orange crystalline product started to appear after a week. Evaporation was continued until the solvent approached the solid product (yield 0.15 g, 29%). *Procedure 3*: A 0.29 g (0.60 mmol) sample of *cis*-Ru(dmsO)₄Cl₂ was dissolved in 20 mL sodium acetate buffer (0.5 M, pH 4.8) followed by addition of 0.5 g (0.20 mmol) of Cs₆[P₂W₅O₂₃]·18H₂O. This solution was refluxed for 15 min and then cooled to room temperature. The solution was filtered and then allowed to evaporate in an open beaker at room temperature. An orange crystalline product started to appear after a week. Evaporation was continued until the solvent approached the solid product (yield 0.1 g, 24%). IR for Cs₄Na₂[HPW₇O₂₈Ru(dmsO)₃]·12H₂O (**1a**): 1433(w), 1408(w), 1321(w), 1301(w), 1099(s), 1075(sh), 1023(m), 945(m), 926(s), 896(s), 867(s), 849(sh), 794(s), 729(sh), 689(s), 623(w), 525(w), 430(w) cm⁻¹. Anal. Calcd (Found) for **1a**: Cs 18.4 (17.6), Na 1.6 (1.7), Ru 3.5 (3.2), W 44.4 (44.9), P 1.1 (1.2), S 3.3 (2.9), C 2.5 (2.5), H 1.5 (1.8)%.
- 20 A 0.14 g (0.29 mmol) sample of *cis*-Ru(dmsO)₄Cl₂ was dissolved in 20 mL sodium acetate buffer (0.5 M, pH 6.5) followed by addition of 0.5 g (0.19 mmol) of Na₈H[A-AsW₉O₃₄]·11H₂O. This solution was heated to 50 °C for 1 h and then cooled to room temperature. The solution was filtered and then 0.5 mL of 1.0 M CsCl solution was added. This solution was allowed to evaporate in an open beaker at room temperature. An orange crystalline product started to appear after a week. Evaporation was continued until the solvent approached the solid product (yield 0.32 g, 64%). IR for Cs₂Na₄[HAsW₇O₂₈-Ru(dmsO)₃]·8H₂O (**2a**): 1426(w), 1407(w), 1317(w), 1300(w), 1112(m), 1086(w), 1019(m), 963(sh), 937(m), 883(s), 863(s), 842(s), 791(m), 725(sh), 685(s), 621(sh), 521(w), 483(w), 429(w) cm⁻¹. Anal. Calcd (Found) for **2a**: Cs 10.0 (10.6), Na 3.5 (3.3), Ru 3.8 (3.6), W 48.6 (47.9), As 2.8 (2.5), S 3.6 (3.6), C 2.7 (2.5), H 1.3 (1.5)%.
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- 22 Solution NMR (D₂O, 20 °C) for Cs₂Na₄[HAsW₇O₂₈Ru(dmsO)₃]·8H₂O (**2a**): ¹⁸³W, δ -85.2(singlet, 2W), -100.9(singlet, 2W), -154.2 (singlet, 2W), -155.1(singlet, 1W) ppm; ¹³C, δ 43.6(singlet, 2C), 44.1(singlet, 2C), 44.2(singlet, 2C) ppm; ¹H, δ 3.22(singlet, 6H), 3.28(singlet, 6H), 3.38(singlet, 6H) ppm.