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A novel isopolytungstate functionalized by ruthenium: $[HW_9O_{33}Ru^{II}_2(dmso)_6]^{7-}$

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The ruthenium-supported isopolyanion $[HW_9O_{33}Ru^{II}_2(dmso)_6]^{7-}$ (1) is composed of a nonatungstate wheel stabilized by two $Ru(dmso)_3$ groups, representing the first structurally characterized Ru-coordinated polyoxotungstate and a novel class of isopolyanions supporting photochromic moieties.

Polyoxometalates have been known for more than 200 years, but they are still an emerging class of compounds.[1] This is mostly due to their unique structural variety and the associated multitude of properties.[2–3] There have been increasing efforts worldwide towards the surface functionalization of polyoxometalates by organic or organometallic species with the aim of generating new hybrid materials. A variety of approaches have been used to covalently link organic or organometallic moieties to polyoxoanions.[4–7] Also ruthenium-substituted polyoxometalates are of interest, which is mostly due to the highly redox-active nature of ruthenium which allows one to envision catalytic applications.[8] In the last couple of years especially Neumann *et al.* have engaged in a large number of studies on the catalytic properties of ruthenium-containing polyanion salts.[9] However, the number of structurally well-characterized ruthenium-substituted polyoxomolybdates[10] and polyoxotungstates[11] is extremely small. This is mostly due to the lack of a pure, well-characterized, water-soluble, air-stable and labile Ru-precursor. Over the last decade or so the organometallic ruthenium(II) complex, *cis*-$Ru(dmso)_4Cl_2$, has become the standard ruthenium precursor worldwide for the synthesis of ruthenium-substituted polyoxoanions.[12]

Single crystal X-ray analysis on $Na_7[HW_9O_{33}Ru_2((CH_3)_2SO)_6]\cdot 25.5H_2O$ (**Na-1**) revealed the novel polyoxoanion $[HW_9O_{33}Ru^{II}_2(dmso)_6]^{7-}$ (**1**), which is composed of a nonatungstate wheel stabilized by two $Ru(dmso)_3$ groups (Fig. 1).† In **1** three edge-shared W_3O_{13} triads are linked to each other *via* corner-sharing leading to a cyclic structure. This tungsten–oxo fragment has never been observed before and therefore **1** represents the first member of a novel class of isopolyanions. Furthermore polyanion **1** contains the first nona-isopolytungstate and the first cyclic isopolytungstate assembly known to date. Polyanion **1** also represents the first structurally characterized polyoxotungstate assembly to which a ruthenium–dmso fragment is grafted.

The ruthenium centers are coordinated to three oxo-groups of the isopolytungstate core and to the sulfur atoms of three terminal dmso ligands. This leads to a trigonal antiprismatic coordination geometry for ruthenium. Very recently Neumann *et al.* have observed exactly the same $Ru(dmso)_3$ fragment bound to a novel heptamolybdate species.[10d]

Polyanion **1** was synthesized in a simple one-pot procedure in aqueous, buffered medium.[13] However, **1** can also be synthesized in pure water and it is stable over a very large pH range (pH 2–7) as shown by NMR and IR.

Interestingly **Na-1** crystallized in the chiral space group R_3 although neither **1** nor the counterions (Na^+) are intrinsically chiral. The chirality must have been imposed by solid state packing. The asymmetric unit of **1** contains two Ru(dmso) groups and a W_3O_{13} triad (Fig. 2), indicating crystallographic C_3 symmetry for **1**. However, we have shown by NMR (see below) that this polyanion has nominal D_{3h} symmetry in solution.

Bond valence sum calculations indicate that none of the terminal or μ_2-bridging oxygens in **1** is protonated.[14] However, the bond valence sum for the unique μ_3-oxygen O_{123} is $s = 1.56$, which is in between the values expected for an oxo ($s = 2$) and a hydroxo group ($s = 1$). Considering that only one W_3O_{13} triad is present in the asymmetric unit the remaining two μ_3-oxygens O_{123}' and O_{123}'' are generated by symmetry. This means that we observe average bond distances for O_{123} resulting in average bond valence sums. We believe that one of the three O_{123} atoms in **1** is monoprotonated whereas the other two are oxo-groups. This should lead to an average bond valence sum of $s = 1.66$, which is very close to the observed value of $s = 1.56$. Furthermore, this view is also supported by the distances between O_{123}, O_{123}', and O_{123}'' which are 2.80(1) Å in all cases, indicating hydrogen bonding. We hope that future neutron diffraction studies will support these conclusions.

We also examined the solution properties of **1** by ^{183}W-NMR (D_2O, 20 °C) and discovered two signals at −141.8 and −166.3 ppm with a ratio of 2 : 1. This is in complete agreement with the solid state structure of **1**, which indicates the presence of two groups of chemically inequivalent tungsten nuclei (W1/W2 and W3) in a 2 : 1 ratio. Interestingly we observed two ^{13}C-NMR (D_2O, 20 °C) peaks at 45.2 ppm and 45.6 ppm and also two ^{1}H-NMR (D_2O, 20 °C) peaks at 3.2 ppm and 3.6 ppm, respectively. These results are consistent with each other and indicate the presence of two types of hydrogen and carbon atoms in **1**. This means that all

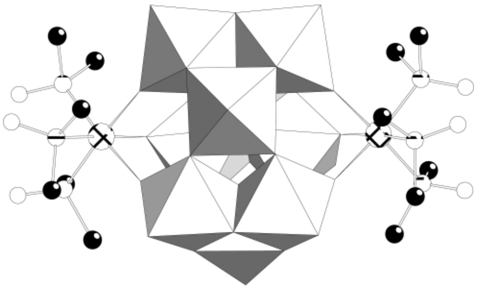

Fig. 1 Combined polyhedral/ball and stick representation of $[HW_9O_{33}Ru^{II}_2(dmso)_6]^{7-}$ (**1**). The octahedra represent WO_6 and the balls are ruthenium (cross-hatched), sulfur (horizontally hatched), carbon (black) and oxygen (white). Hydrogen atoms are omitted for clarity.

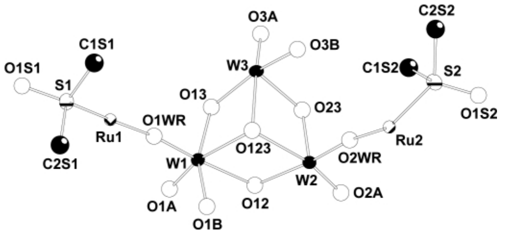

Fig. 2 Ball and stick representation of the asymmetric unit of $[HW_9O_{33}Ru^{II}_2(dmso)_6]^{7-}$ (**1**) showing 50% probability ellipsoids and the labeling scheme.

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six dmso ligands in **1** are magnetically equivalent in solution, but the two methyl groups within each dmso molecule are magnetically inequivalent. The only reasonable explanation for this is hindered rotation of the dmso ligands around the Ru–S bond.

UV–vis spectroscopy studies on an aqueous solutions of **1** show a MLCT band at 368 nm (ε = 11000 $M^{-1}cm^{-1}$), which is red-shifted by 20 nm compared to the precursor *cis*-$Ru(dmso)_4Cl_2$ (348 nm, ε = 460 $M^{-1}cm^{-1}$).[11a] The title compound **1** is not luminescent, but we believe that substitution of one or more dmso ligands by appropriate π-acceptor ligands (*e.g.* bipy) might lead to products with long lived excited states. Furthermore we identified an interesting color change from yellow to brown for solutions of **1** when exposed to sunlight and such solutions show a novel absorption peak at 450 nm. These highly interesting photochromic properties of the title polyanion require further elucidation, especially as we have preliminary NMR and IR evidence that the W_9 core of **1** stays intact.

Close inspection of **1** indicates that removal of the two $Ru(dmso)_3$ groups would result in the hypothetical isopolyanion $[W_9O_{33}]^{12-}$ (**1a**) which is composed exclusively of fused W_3O_{13} triads (Fig. 3). Most likely some degree of protonation is necessary to reduce the charge-density of this species, as none of the isopolytungstates known to date has a charge of −12: $[W_2O_7]^{2-}$, $[W_4O_{16}]^{8-}$, $[HW_5O_{19}]^{7-}$, $[W_6O_{19}]^{2-}$, $[H_3W_6O_{22}]^{5-}$, $[W_7O_{24}]^{6-}$, $[W_{10}O_{32}]^{4-}$, $[H_2W_{12}O_{42}]^{10-}$, α-$[HW_{12}O_{40}]^{7-}$, α-$[H_2W_{12}O_{40}]^{6-}$, β-$[H_2W_{12}O_{40}]^{6-}$ and $[H_6W_{18}O_{60}]^{6-}$.[2,15] Therefore we propose the formula $[H_xW_9O_{33}]^{(12-x)-}$ for the novel species **1a**, which adds a novel structural type to the above list. At the same time **1a** represents the first nonatungstate and the first cyclic isopolytungstate. Polyanion **1a** does not violate the Lipscomb principle as the three equivalent pairs of W-atoms have only two, *cis*-related, terminal oxo ligands.[2] The three unique W-atoms have only one terminal oxo ligand. Although we believe that **1a** can exist as an independent species, we have not been able to isolate it yet. It is not unlikely that an alkali, alkaline earth, or ammonium ion could also occupy each face of **1a** instead of the $Ru(dmso)_3$ groups. This would also reduce the charge of **1a** and at the same time provide additional structural stability.

We believe that numerous derivatives of **1** can be synthesized by (a) replacing the dmso ligands by other mono-, di- and tridentate ligands and (b) substituting the Ru by other transition metal ions and (c) any combinations of a and b. An appropriate choice of terminal ligands could also allow to link several nonatungstate fragments resulting in oligomeric or polymeric assemblies with interesting functions.

We plan to investigate in detail the photochemistry, electrochemistry, magnetic, medicinal and oxidation catalysis properties of **1**. Furthermore we would like to find out if the molybdenum analog of **1** exists.

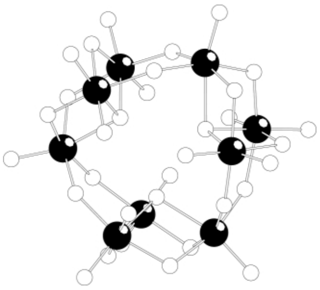

Fig. 3 Ball and stick representation of the tungsten–oxo core of $[HW_9O_{33}Ru^{II}_2(dmso)_6]^{7-}$ (**1**) which represents a novel isopolyanion.

Notes and references

† Crystal data: $Na_7[HW_9O_{33}Ru_2((CH_3)_2SO)_6]\cdot 25.5H_2O$ (**Na-1**): $C_{12}H_{88}Na_7O_{64.5}Ru_2S_6W_9$, M = 3475.38, rhombohedral, R_3, a = 13.1572(6), b = 13.1572(6), c = 40.101(4) Å, V = 6011.9(7) Å^3, T = 200 K, Z = 3, μ(Mo–Kα) = 13.51 mm^{-1}, 20807 reflections collected, 6631 unique (R(int) = 0.066), $R1$ = 0.043, $wR2$ = 0.099 ($I > (2\sigma(I))$. CCDC 234284. See http://www.rsc.org/suppdata/cc/b4/b403902e/ for crystallographic data in .cif format.

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