A new organometallic heteropolytungstate related to $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$: synthesis and structural characterisation of the bis-$\{Ru(p\text{-cymene})\}^{2+}$-containing anion $[Sb_2W_{20}O_{70}\{Ru(p\text{-cymene})\}_2]^{10-}$†

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The easy synthesis of $[Sb_2W_{20}O_{70}\{Ru(p\text{-cymene})\}_2]^{10-}$ by the reaction between the organometallic precursor $[Ru(p\text{-cymene})Cl_2]_2$ and $[Sb_2W_{20}O_{70}]^{14-}$, formed *in situ*, confirms the importance of the organometallic route to well defined ruthenium(+II)-substituted heteropolytungstates.

Due to their known catalytic activity in various oxidation processes,[1] the introduction of noble cations in heteropolyanions has become at present a field of growing interest for the polyoxometalate community.[2–12] Even though recent efforts have been made for the synthesis of palladium or platinum derivatives,[11–13] ruthenium is probably still the platinum-group element that is the most frequently incorporated into a heteropolyoxotungstate structure.[3–10] Nevertheless, no systematic way of synthesising such ruthenium derivatives stems from the literature results. Moreover, most of the recent examples of the noble elements derivatives are based on the assembly of $\{XW_{11}O_{39}\}^{n-}$, $\{P_2W_{17}O_{61}\}^{10-}$ or A-type $\{XW_9O_{34}\}^{q-}$ units, and few compounds built from B-type $\{XW_9O_{33}\}^{r-}$ moieties have been described.[11] Herein, we report on the synthesis and the structural characterisation of the new anion $[Sb_2W_{20}O_{70}\{Ru(p\text{-cymene})\}_2]^{10-}$, which contains two $\{Ru(p\text{-cymene})\}^{2+}$ fragments grafted on B-type $\{SbW_9O_{33}\}^{9-}$ sub-units.

Among the large number of structures described in the chemistry of heteropolytungstates, we considered $K_{12}[X_2W_{22}O_{74}(OH)_2]\cdot 27H_2O$ (X = Sb^{III} (K-**2**), Bi^{III})[13–15] as potentially interesting for the grafting of *fac*-$\{ML_3\}$ $\{Ru(p\text{-cymene})\}^{2+}$ cations onto a polyoxometalate core. Indeed, the anion can be described as the assembly of two β-B-$[XW_9O_{33}]^{9-}$ sub-units linked by four $\{WO_6\}$ octahedra, among which the two external ones display a facial $\{WO_2(OH)\}^+$ arrangement. Morever, recent studies by Krebs and Pope showed that various $M^{n+}(H_2O)_3$ fragments ($M^{n+} = Fe^{3+}, Co^{2+}, Zn^{2+}, Ni^{2+}$) may replace these *fac*-$\{WO_2(OH)\}^+$ moieties to form $[X_2W_{20}O_{70}M_2(OH_2)_6]^{(14-2n)-}$ derivatives.[14,15] The replacement of the *fac*-$\{WO_2(OH)\}^+$ groups in $[X_2W_{22}O_{74}(OH)_2]^{12-}$ by the topologically equivalent $\{Ru(p\text{-cymene})\}^{2+}$ thus appeared as highly attractive. The resulting complex $[Sb_2W_{20}O_{70}\{Ru(p\text{-cymene})\}_2]^{10-}$ (**1**) was in fact first obtained by a self-assembly reaction from a mixture of $Na_2WO_4\cdot 2H_2O$, Sb_2O_3 and $[Ru(p\text{-cymene})Cl_2]_2$ in a W : Sb : Ru ratio of 10 : 1 : 1 in water.‡ After its isolation as a sodium salt, the complex was characterised by chemical analysis, spectroscopic methods (IR and multinuclear NMR: ^1H, ^{13}C, ^{183}W)§ and single-crystal X-ray structure analysis.¶

The unit cell contains two crystallographically independent anions $[Sb_2W_{20}O_{70}\{Ru(p\text{-cymene})\}_2]^{10-}$, which are located on inversion centres. The structure of one of the anions **1** is depicted in Fig. 1. As it is usually observed in such situations,[16] the two crystallographically-independent anions present very similar metrical parameters. Even if there are no crystallographically-imposed symmetry elements, except for the inversion centre, the Ru, Sb, and W1 atoms are nearly coplanar. They define a pseudo-plane of symmetry through which W2 and W3, W4 and W7, W5 and W6, W8 and W9 respectively become symmetry-equivalent. Consequently, the $[Sb_2W_{20}O_{70}\{Ru(p\text{-cymene})\}_2]^{10-}$ anions achieve a nearly C_{2h} symmetry. The Ru^{II} cation achieves an 18-electron configuration through coordination to three oxygen atoms of two β-B-$[SbW_9O_{33}]^{9-}$ units. The Ru–O distances are in the range of 2.09–2.17 Å and are comparable to those observed in previously reported $\{Ru^{II}(arene)\}$-containing polyoxometalates.[17,18]

According to the anion formula, ten cations are required to ensure electroneutrality, but single-crystal X-ray structure determination only allowed the location of eight sodium cations in general positions, plus one cation on an inversion center. This is not unprecedented for highly hydrated alkaline salts of polyoxometalates for which i) some cations can be statistically distributed over the structure and ii) sodium cations may be hardly discernable from water molecules. In our case, forty two water molecules were located by X-ray spectroscopy. According to the results obtained by sodium atomic spectroscopy and carbon and hydrogen elemental analyses, the most accurate formula appeared to be $Na_{10}[Sb_2W_{20}O_{70}\{Ru(p\text{-cymene})\}_2]\cdot 42H_2O$.

The infrared spectrum of **1** is closely related to that of the parent compound **2** in the range of 350–1000 cm^{-1} with the notable exception of a 10 cm^{-1} shift to low wavenumbers of the strong $W{=}O_t$ bands. This effect is a common feature already observed for lacunary and metal-substituted POM derivatives by comparison with their parent saturated analogues, and has been assigned to the weakening of the framework cohesion through lacunarisation, leading to a decrease of the stretching force constants.[19] Such a shift had already been observed for the cobalt derivative $[Sb_2W_{20}Co_2O_{70}(OH_2)_6]^{10-}$.[14]

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† Electronic supplementary information (ESI) available: ^1H and ^{13}C NMR spectra of **1**; view of the symmetry elements in **1**. See DOI: 10.1039/b510300b

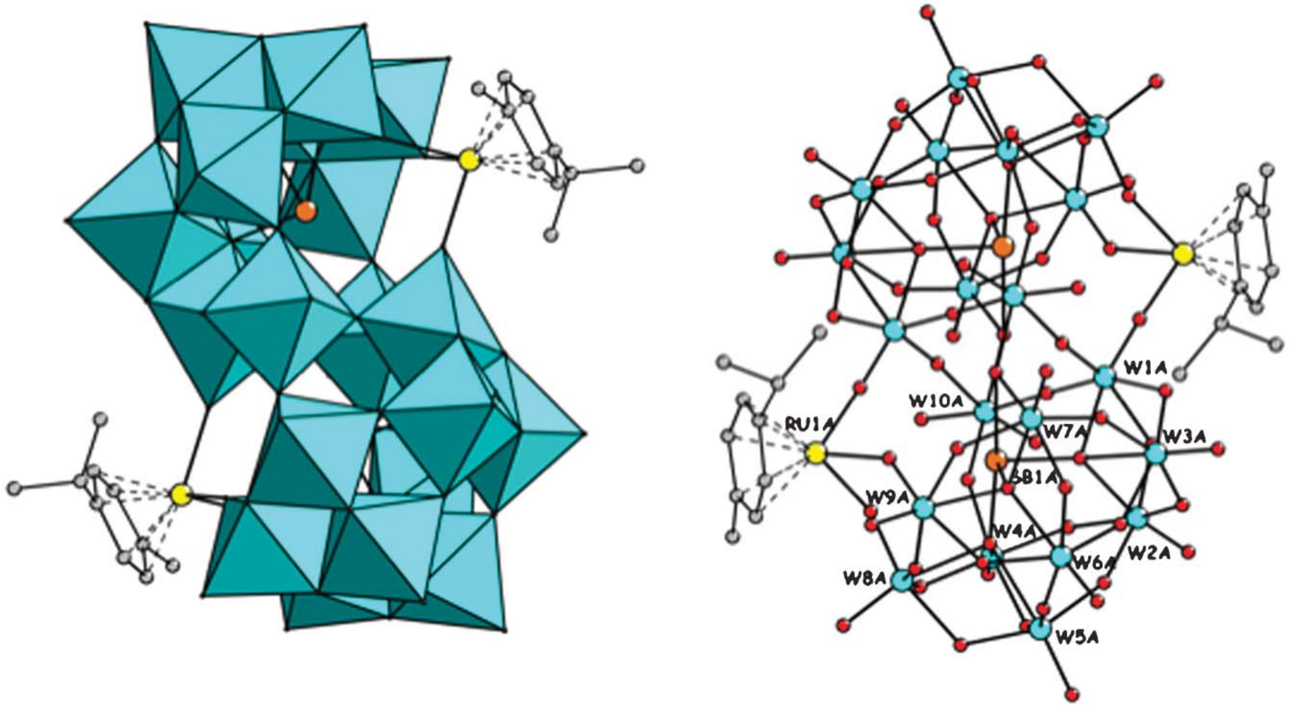

Fig. 1 Polyhedral (left) and ball and stick (right) molecular representations of $[Sb_2W_{20}O_{70}\{Ru(p\text{-cymene})\}_2]^{10-}$ (**1**).

The ^1H and ^{13}C NMR spectra of **1** both display only one set of signals for the two equivalent *p*-cymene ligands.[17] The ^{183}W NMR spectrum of a 0.05 mol L^{-1} solution of Na-**1** in D_2O (Fig. 2) reveals the presence of five lines with a 2 : 2 : 4 : 1 : 1 relative intensity. The strongest line actually splits into two resonances after resolution enhancement, and corresponds therefore to the accidental degeneracy of two signals with relative intensity of 2. This spectrum is in accordance with the conservation of the C_{2h} symmetry of the oxometallic framework in solution, due to the conservation of both the inversion centre and the symmetry plane described above. This implies that in solution, either the *p*-cymene rings are reoriented in such a way that both C_{CH_3}–$C_{CH(CH_3)_2}$ axes lie in the plane defined by the two ruthenium and the two antimony atoms, or that their rotation around the {Ru(arene)} axis is very rapid. Although both explanations are consistent with the ^1H and ^{13}C NMR spectra, the latter is more likely, insofar as it has already been noted for {Ru(arene)}-derivatives of polyoxometalates.[18] The broad signal ($\Delta\nu_{1/2}$ = *ca.* 80 Hz) of relative intensity 1 with the lowest chemical shift (−322 ppm) may be attributed to the peculiar tungsten atoms W10 (*cis*-WO_2 groups) which connect the two $\{SbW_9Ru\}$ sub-units.[20] Therefore the second signal of relative intensity 1 (at δ = −169 ppm) has to be assigned to the tungsten atoms W1 lying in the pseudo plane of symmetry containing also the two Ru and Sb atoms. Because of the lack of observable tungsten–tungsten satellites, no attempt was made to assign the other lines.

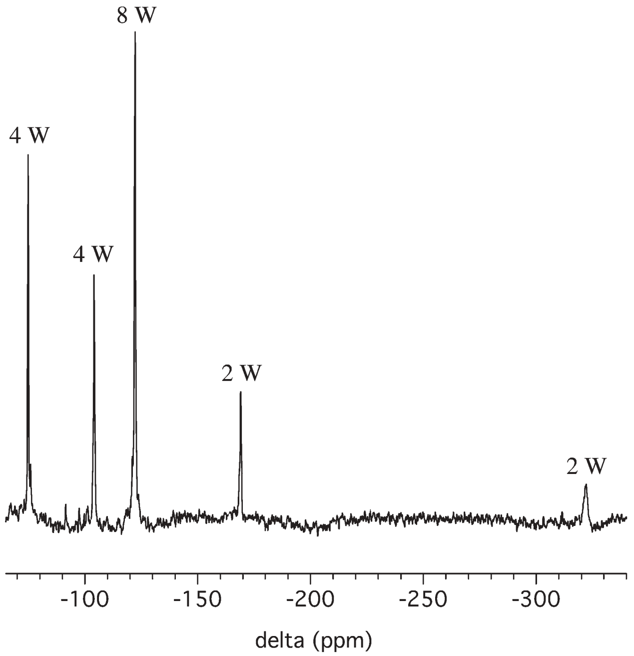

Fig. 2 20.8 MHz ^{183}W NMR spectrum of a 0.05 M solution of **1** in D_2O (*ca.* 10 000 transients; total spectrometer time 19 h). Chemical shifts are given with respect to 2 M Na_2WO_4 in D_2O at pD = 10.

Furthermore, we checked by ^{183}W and ^{13}C NMR spectroscopies that the synthesis of **1** can also occur by reaction of an equimolar mixture of **2** and $[Ru(p\text{-cymene})(Cl_2)]_2$ in water at pH = 6.0. According to Krebs's description of the reactivity of **2**, the formation of **1** can be attributed to the evolution of **2** into the non-isolated "lacunary" anion $[Sb_2W_{20}O_{70}]^{14-}$, on which two $\{Ru(p\text{-cymene})\}^{2+}$ fragments coordinate. The ^{13}C spectrum of the solution reveals that **1** is the main species in solution. The corresponding ^{183}W NMR spectrum exhibits, apart from the signals previously attributed to **1**, other minority signals, which may be due to the presence of polyoxotungstate frameworks formed from the tungstate fragments which were liberated in solution by evolution of **2**.‖

During the last decade, several groups have tried to generalise the obtention of ruthenium derivatives of heteropolytungstates.[4–10] We showed in a recent study that the reactivity of $[Ru^{II}(arene)Cl_2]_2$ complexes allowed the formation of $[\alpha\text{-}PW_{11}O_{39}]^{7-}$-based complexes.[17] Herein, the easy formation of anion **1** either by a self-assembly method or by a substitution reaction on the complete anion $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$ (**2**) confirms that the organometallic $[Ru^{II}(arene)Cl_2]_2$ complexes are good precursors to such derivatives. In a qualitative way, one important parameter was the complementarity between the geometry of the lacuna of $[Sb_2W_{20}O_{70}]^{14-}$ and the ruthenium arene fragment. More generally, it appears that the diamagnetic *fac*-$\{Ru^{II}L_3\}$-containing complexes, with L_3 = arene or $(dmso)_3$, are the most widely used precursors, despite the known inertness of low spin d^6 cations.

Notes and references

‡ Synthesis of **1**: to a solution of $Na_2WO_4 \cdot 2H_2O$ (5.32 g, 16 mmol) in 30 mL of water was added 0.235 g (0.80 mmol) of Sb_2O_3 dissolved in 0.5 mL of concentrated HCl. The pH of the solution, initially close to 9.0, was adjusted to 5.2 with concentrated HCl. $[Ru(p\text{-cymene})Cl_2]_2$ (0.439 g, 0.80 mmol) was added and the solution was refluxed for one hour then cooled to room temperature. The pH was then adjusted to 4.4 and maintained at this value with concentrated HCl. The solution was allowed to stand at room temperature for several weeks, during which red crystals of Na-**1** formed. These crystals were filtered on a frit glass (yield: 0.650 g, 13%). A few uncoloured crystals of NaCl also formed and could easily be separated. Elemental analysis calcd for $C_{20}H_{112}Na_{10}O_{112}Ru_2Sb_2W_{20}$, C 3.70, H 1.74, Na 3.54, found: C 3.67, H 1.54, Na 3.43.

§ ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.27$ (d, 4H, Ar-*H*, $^3J = 6.0$ Hz), 5.67 (d, 4H, Ar-*H*, $^3J = 6.0$ Hz), 3.11 (h, 2H, Ar-C*H*-$(CH_3)_2$, $^3J = 6.9$ Hz), 2.41 (s, 6H, Ar-CH_3), 1.46 (d, 12H, Ar-CH-$(CH_3)_2$, $^3J = 6.9$ Hz). ^{183}W NMR (20.83 MHz, H_2O/D_2O) : $\delta = -322$ (s, 2W), -169 (s, 2W), -122.2 (s, 8W), -104 (s, 4W), -74.8 (s, 4W). ^{13}C NMR (75.47 MHz, H_2O/D_2O): $\delta = 98.52$ (s, 2C), 96.81 (s, 2C), 83.90 (s, 4C), 75.87 (s, 4C), 30.93 (s, 2C), 22.48 (s, 4C), 16.92 (s, 2C). IR (KBr pellet, ν/cm^{-1}), 948 (m), 872 (sh), 831 (s), 803 (s), 762 (s), 658 (m), 351 (m).

¶ *Crystal data for* Na-**1**: $C_{20}H_{113.5}Na_{8.5}O_{112}Ru_2Sb_2W_{20}$, $M = 6464.66$, triclinic, space group $P\bar{1}$ (no. 2), $a = 15.914(6)$, $b = 15.932(5)$, $c = 24.166(9)$ Å, $\alpha = 100.88(3)$, $\beta = 92.11(3)$, $\gamma = 97.96(3)°$, $V = 5946(4)$ Å^3, $Z = 2$, $D_c = 3.610$ g cm^{-3}, $\mu = 20.094$ mm^{-1}. Data collection ($1 < 2\theta < 25°$) was performed at 295 K, on an Enraf-Nonius CAD4 diffractometer (Mo-Kα = 0.71073 Å). The structure was refined on F^2 and converged for 19499 unique reflections (11326 with $I > 2\sigma(I)$) and 823 parameters to give $R = 0.0632$ and Rw $(F^2) = 0.1961$ (all data). Residual electron density = -3.47 e$^-$ Å^{-3} (min) -3.65 e$^-$ Å^{-3} (max). The two maximum residual density peaks were located at 1.200 Å from W9B and 1.080 Å from W10A. Only the Ru, W, and Sb atoms were refined anisotropically. No hydrogen atoms were located. CCDC 265419. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b510300b

‖ This synthetic method allowed us to obtain a mother liquor in which **1** is nearly the only organometallic species present. However attempts to isolate a pure sample of **1** in the solid state by addition of various alkaline cations to the solution led to mixtures of **1** and unidentified by-products. So far, only the self-assembly method has allowed us to obtain pure samples of **1** in the solid state.

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