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Syntheses and characterization of the heptasodium salt of the Keggin-type triniobium-substituted polyoxoanion $SiW_9Nb_3O_{40}^{7-}$ and the all-sodium salt of the polyoxoanion-supported organometallic complex $[(\eta^5\text{-}C_5Me_5)Rh \cdot SiW_9Nb_3O_{40}]^{5-}$

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Abstract

The preparations of A-β-$Na_7SiW_9Nb_3O_{40}$ and $Na_5[(\eta^5\text{-}C_5Me_5)Rh \cdot SiW_9Nb_3O_{40}]$ are described. The water-soluble form of the Keggin-type trisubstituted heteropolyanion, A-β-$SiW_9Nb_3O_{40}^{7-}$, of interest as a polyoxoanion support for organometallic complexes, was isolated in pure form in 61% yield as its heptasodium salt with 16 waters of hydration. The polyoxoanion-supported organometallic complex as its all-sodium salt, $[(\eta^5\text{-}C_5Me_5)Rh \cdot SiW_9Nb_3O_{40}]^{5-}$ was obtained in 21% yield as an analytically pure, homogeneous yellow-brown solid by the reaction of $[(\eta^5\text{-}C_5Me_5)Rh(CH_3CN)_3]^{2+}$ with the trisubstituted heteropolyanion $SiW_9Nb_3O_{62}^{7-}$ in CH_3CN–DMSO. These all-sodium salts have required their own novel preparations and purifications, and have never been derived directly from the known all-Bu_4N^+ salts of the corresponding Keggin heteropolyanions. Compositional characterization was accomplished by complete elemental analyses, TG/DTA, and FT-IR. Structural characterization in solution was achieved by combination of ^1H, ^{13}C and ^{183}W NMR spectroscopies.

Keywords: Rhodium; Sodium; Niobium; Tungsten; Polyoxometallate; Keggin-type

1. Introduction

Recently, we reported the syntheses and isolations of the nonasodium salt of the Dawson-type triniobium-substituted polyoxoanion B-α-$P_2W_{15}Nb_3O_{62}^{9-}$ [1] and the heptasodium salt of the polyoxoanion-supported organometallic complex $[(\eta^5\text{-}C_5Me_5)Rh \cdot P_2W_{15}Nb_3O_{62}]^{7-}$ [2]. That work was aimed at providing a water-soluble form of the important $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion [1,3–5] and at extending the concept of water solubility and all-inorganic composition to $[(\eta^5\text{-}C_5Me_5)Rh \cdot P_2W_{15}Nb_3O_{62}]^{7-}$ [2,3,6]. From the synthetic point of view, isolation of these all-sodium salts has required their own preparation and purification, including choice of the appropriate solvent system. Prior to that work, the $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion had been available only as its organic-solvent soluble (and water-insoluble) all TBA$^+$ salt [3], TBA = $[(n\text{-}C_4H_9)_4N]^+$.

Hence, the all-sodium salt of $P_2W_{15}Nb_3O_{62}^{11-}$ extended the well-documented organometallic chemistry of $P_2W_{15}Nb_3O_{62}^{9-}$ into aqueous media (see for example Refs. [1,4,6] and references cited therein). In a separate account, the full details of the synthesis and isolation of the polyoxoanion-supported organometallic complex $[(\eta^5\text{-}C_5Me_5)Rh \cdot P_2W_{15}Nb_3O_{62}]^{7-}$ as its all-TBA$^+$ salt have been reported [1–8].

The goal of the present work is to apply the concepts of water-solubility and all-inorganic composition to the triniobium-substituted Keggin-type polyoxoanion and to its supported organometallics, specifically to the Keggin-type polyoxoanion A-β-$SiW_9Nb_3O_{40}^{7-}$ (Fig. 1(A)) and its organometallic complex, $[(\eta^5\text{-}C_5Me_5)Rh \cdot SiW_9Nb_3O_{40}]^{5-}$ (Fig. 1(B)) [10,11].

In earlier work by Finke and co-workers, focused on polyoxoanion-supported complexes, the syntheses and isolations of such compounds as their organic-solvent soluble and water-insoluble forms in all-TBA$^+$ salts had been reported [5,11]. In the Keggin-type polyoxoanion, three niobium atoms are substituted in the A-site of

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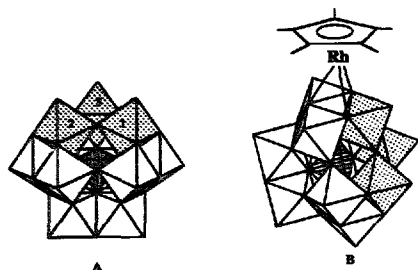Fig. 1. (A) Polyhedral representation of the Keggin-type heteropolyanion β-1,2,3-$SiW_9Nb_3O_{40}^{7-}$. The three niobium atoms are represented by hatched octahedra in the 1–3 positions (A-site). The WO_6 octahedra occupy the white octahedra, and an SiO_4 group is shown as the internal tetrahedron. (B) One of the two most plausible C_s symmetry structures of $[(\eta^5-C_5Me_5)Rh \cdot SiW_9Nb_3O_{40}]^{3-}$. The other most plausible structure involves bonding of the organometallic moiety to two bridging W–O–Nb oxygens and a terminal Nb=O oxygen [9].

the β-Keggin structure, and in its polyoxoanion-supported complex, the organometallic group $[(\eta^5-C_5Me_5)Rh]^{2+}$ is bonded to two bridging W–O–Nb oxygen atoms and a bridging W–O–W oxygen occupying the B-site of the $SiW_9Nb_3O_{40}^{7-}$ Keggin-type polyoxoanion, as shown by solution spectroscopic methods [10–12].

Reasons for the synthesis of all-sodium salts of Keggin-type polyoxoanion and its polyoxoanion-supported complexes include: (a) their anticipated water-solubility, thereby bringing polyoxoanion-organometallic complexes and their reactivity into water (vide supra), (b) the potential of all-inorganic basic polyoxoanions as novel types of solid-base heterogeneous catalysts, and (c) the possibility that such all-inorganic, water soluble salts might provide a more general route to crystalline $SiW_9Nb_3O_{40}^{7-}$-supported organometallic catalyst precursors [13].

Herein we report the full details of the syntheses and isolations of the all-sodium salt, $Na_7SiW_9Nb_3O_{40} \cdot 16H_2O$ (1) in 61% yield (on an 11 g scale) and $Na_3[(\eta^5-C_5Me_5)Rh \cdot SiW_9Nb_3O_{40}] \cdot 3DMSO \cdot 2H_2O$ (2) in 21% yield (0.33 g scale). Also reported are the compositional characterizations of 1 and 2 by full elemental analyses, FT-IR, TG/DTA and their structural characterization in solution by ^1H, ^{13}C and ^{183}W NMR spectroscopies.

2. Experimental

2.1. Chemicals

The following were used as-received: $NaBF_4$, $NaOH$, $AgBF_4$, CH_3CN, DMSO, EtOAc, Et_2O, 3A molecular

sieves (all from Wako); DMSO-d_6 (Aldrich). $[(\eta^5-C_5Me_5)RhCl_2]_2$ [3,14,15] and $[(n^5-C_4H_9)_4N]_6H_2Si_2W_{18}Nb_6O_{77}$ [11] were prepared according to the literature.

2.2. Instrumentation / analytical procedures

Elemental analyses were obtained from Mikroanalytisches Labor Pascher (Remagen, Germany). Infrared spectra were recorded on a Nicolet 510 FT-IR spectrometer in KBr disks at room temperature. Thermogravimetric (TG) and differential thermal analyses (DTA) were acquired using a Rigaku TAS 300 TG 8101D. TG/DTA were run under air with a temperature ramp of $1 \,^{\circ}C \, min^{-1}$ between 20 and 500 °C.

^1H NMR (399.65 MHz) and ^{13}C NMR (100.40 MHz) were recorded at 22 °C in 5 mm o.d. tubes on a Jeol JNM-EX 400 FT-NMR spectrometer and Jeol EX-400 NMR data processing system. ^1H NMR and ^{13}C NMR spectra were referenced to an internal standard of $(CH_3)_4Si$ (TMS). Chemical shifts are reported on the δ scale and resonances downfield of TMS (δ 0) are recorded as positive. ^{183}W NMR (16.50 MHz) spectra were recorded at 22 °C in 10 mm o.d. tubes on a Jeol JNM-EX 400 FT-NMR spectrometer equipped with a Jeol NM-40T10L low-frequency tunable probe and a Jeol EX-400 NMR data processing system. These spectra were referenced to an external standard of saturated Na_2WO_4–D_2O solution by the substitution method. Chemical shifts are reported on the δ scale with resonances upfield of Na_2WO_4 (δ 0) as negative.

2.3. Synthesis of A-β-$Na_7SiW_9Nb_3O_{40} \cdot 16H_2O$ (1)

5.00 g (0.756 mmol) of $(Bu_4N)_6H_2Si_2W_{18}Nb_6O_{77}$ [11] was dissolved in 50 ml CH_3CN in 200 ml conical beaker at 50–60 °C, with stirring. At this temperature, to the clear CH_3CN solution, 0.498 g (6 equivalents, 4.536 mmol) of solid $NaBF_4$ was added, which was completely dissolved after about 20 min stirring. To this homogeneous solution at room temperature, exactly 12.11 ml (8 equivalents, 6.05 mmol) of 0.5 M NaOH aqueous solution was added dropwise. In the early stage of this addition, the solution became cloudy, then a white precipitate formed, and finally an oily material appeared at the bottom of the beaker. The stirring was continued, while about 300 ml of CH_3CN was added in three portions. After this addition was over, the stirring was continued for 30 min, and then the conical beaker was let stand for 3 days in the refrigerator. In the bottom of the beaker an oily material collected and the supernatant looked colloidal. While the conical beaker was kept cold, the mother liquor was discarded by decanting, and then the residual material was washed with small amounts of CH_3CN (3 × ca. 10 ml). The sample, still in the conical beaker, was dried overnight in a

55°C oven. The dried material in the conical beaker was redissolved at 50–60°C in ca. 30 ml of pH 8 un-buffered aqueous solution, and the second reprecipitation using ca. 300 ml of CH_3CN and the work-ups were repeated as above. Yield: 2.9 g (63%) of white powder which is soluble in water, slightly soluble in DMSO, but insoluble in CH_3CN, ethyl acetate and ether. This procedure was also effective to a four-times scale-up experiment, resulting in an 11.3 g yield (61%).

2.3.1. Microanalysis

Found: H, 1.07; Na, 5.59; Nb, 9.10; O, 27.8; Si, 0.96; W, 54.0; total: 98.5%. Calc. for $H_{32}Na_7SiW_9Nb_3O_{56}$ or $Na_7SiW_9Nb_3O_{40} \cdot 16H_2O$: H,

Fig. 3. ^{183}W NMR spectra of (a) $Na_7SiW_9Nb_3O_{40}$ in D_2O and of (b) $Na_5[(\eta^5\text{-}C_5Me_5)Rh \cdot SiW_9Nb_3O_{40}]$ in DMSO-d_6, both with reference to an external Na_2WO_4 saturated in D_2O by a substitution method. In spectrum (a), the observed two-line spectrum with 2:1 intensity ratio shows that the complex has C_{3v} (pseudo) symmetry on the ^{183}W NMR time scale. In contrast, in spectrum (b), the observed five-line spectrum shows that the complex has C_s (pseudo) symmetry on the ^{183}W NMR time scale.

1.06; Na, 5.28; Nb, 9.14; O, 29.4; Si, 0.92; W, 54.2%. TG/DTA· weight loss of 9.40% between 47 and 500°C with an endothermic point at 91.0°C. Calc. for $Na_7SiW_9Nb_3O_{40} \cdot 16H_2O$, 9.45% (16$H_2O$). Separately, the same compound was dried overnight at room temperature under reduced pressure (ca. 10^{-3} to 10^{-4} Torr) before analysis. Found: H, 0.30; Na, 5.73; Nb, 9.90; O, 24.4; Si, 1.04; W, 58.2; total: 99.6%. Calc. for $H_8Na_7SiW_9Nb_3O_{44}$ or $Na_7SiW_9Nb_3O_{40} \cdot 4H_2O$: H, 0.28; Na, 5.68; Nb, 9.83; O, 24.8; Si, 0.99; W, 58.4%. IR (KBr), (Fig. 2(a)): 959, 921, 884, 794 cm^{-1}. ^{183}W NMR spectrum (D_2O adjusted to pD 8.4, [1] 295 K), (Fig. 3(a)): $\delta - 121.2$ (6W, $^2J_{W-O-W} = 15.0$ Hz); -127.3 (3W, $^2J_{W-O-W} = 15.0$ Hz).

2.4. Synthesis of $Na_5[(\eta^5\text{-}C_5Me_5)Rh \cdot SiW_9Nb_3O_{40}] \cdot 3DMSO \cdot 2H_2O$ (2)

Finely ground $Na_7SiW_9Nb_3O_{40} \cdot 16H_2O$ (1.50 g; 0.49 mmol) was placed in a 100 ml three-neck round-bottomed flask. Next, 24.0 ml of CH_3CN (dried over molecular sieves) at once and exactly 7.2 ml of DMSO (dried over molecular sieves) were added dropwise while vigorously stirring with a magnetic stir bar. Using a long needle, dry N_2 was passed through the resulting

Fig. 2. FT-IR spectra, measured in KBr disks, of (a) $Na_7SiW_9Nb_3O_{40} \cdot 16H_2O$, (b) $Na_5[(\eta^5\text{-}C_5Me_5)Rh \cdot Si_2W_9Nb_3O_{40}] \cdot 3DMSO \cdot 2H_2O$ (c) $(Bu_4N)_7SiW_9Nb_3O_{40}$, and (d) $(Bu_4N)_5[(\eta^5\text{-}C_5Me_5)Rh \cdot SiW_9Nb_3O_{40}]$. The observation of the characteristic Keggin-type polyoxoanion IR bands between 1100–700 cm^{-1} demonstrates that the $SiW_9Nb_3O_{40}$ support-ion remains intact under the conditions of the synthesis. In spectra (a) and (c), the intense and characteristic 690 cm^{-1} band, due to the vibration of three bridging Nb–O–Nb linkages present in the dimeric polyoxoanion $Si_2W_{18}Nb_6O_{77}^{8-}$ [11], disappears. In spectrum (b), very weak and broad bands consisting of many weak peaks are observable between 1465–1384 cm^{-1}; these are attributed to the vibrations of the supported $(\eta^5\text{-}C_5Me_5)Rh^{2+}$ moiety. In contrast, these bands are obscured in (d) by the very intense C–H vibrations of the Bu_4N^+ countercations.
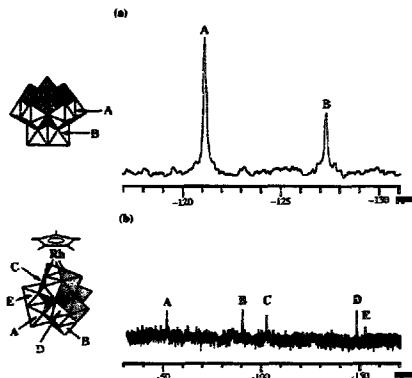
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[1] The pD was calculated from the measured pH (apparent) by pD = pH + 0.4 [16].

Table 1
Chemical shifts of ^1H and ^{13}C NMR spectra for the mixture of positional isomers and for the single isomer

	δ (DMSO-d_6)	
	^1H NMR	^{13}C NMR
Mixture of positional isomers	1.70; 1.73; 1.76	8.25; 8.61; 8.78; 92.6; 96.7; 97.0; 97.7
Single isomer	1.76	8.36; 92.6

suspension for 30 min. In a separate beaker, $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ (0.15 g; 0.25 mmol) was slurried in 6 ml of dry CH_3CN. Solid $AgBF_4$ (0.19 g; 0.98 mmol; 4 equivalents) was added to the slurry causing the immediate formation of an AgCl precipitate. The mixture was stirred for 10 min via a magnetic stir bar, and then filtered through a medium glass frit directly into the stirred suspension of $Na_7SiW_9Nb_3O_{40}$. The precipitate on the glass frit was washed with ca. 4 ml of CH_3CN using a pipette and the washings were also introduced to the heteropolyoxoanion suspension. Thus, the DMSO + CH_3CN solvent mixture used was a total of 7.2 ml + 34 ml. Upon introduction of the in situ generated yellow-orange $[(\eta^5\text{-}C_5Me_5)Rh(CH_3CN)_3](BF_4)_2$ solution, the color of the heteropolytungstate changed from white to yellow-orange. The resulting suspension was stirred under an N_2 stream (with the N_2 inlet needle being above the solution) at 84 °C for 4 h; during this time the yellow-orange color became more intense. After allowing the reaction mixture to cool to room temperature, the yellow-orange precipitate was collected on a medium glass frit, washed three times with ca. 20 ml of CH_3CN, then washed three times with ca. 20 ml of ether and dried in vacuo for several hours at room temperature. The yield at this stage was ca. 0.73 g. (This precipitate contains a mixture of $Na_5[(\eta^5\text{-}C_5Me_5)Rh \cdot SiW_9Nb_3O_{40}]$ and $NaBF_4$. It was shown by ^1H NMR (Table 1) in DMSO-d_6 that the Na_5 salt at this stage still consisted of some positional isomers of the supported $(\eta^5\text{-}C_5Me_5)Rh^{2+}$ group. Longer time reactions (more than 4 h) at 84 °C, which were tried in order to convert such positional isomers to a single isomer, resulted in a decomposition of the target compound. This is attributed to water present in the reaction system which originates from the hydrated form of the starting $Na_7SiW_9Nb_3O_{40}$.) Next, the dry material was transferred to a 50 ml beaker and ca. 5 ml of dry DMSO were added. The resulting cloudy orange solution was filtered through a folded filter paper (Whatman No. 5) into a 100 ml three-neck round-bottomed flask. The yellow-orange filtrate was stirred under an N_2 stream (with the N_2 inlet needle being above solution) at 84 °C for 3 h; during the stirring the yellow-orange color became red. It was shown by ^1H NMR (Table 1) that during this procedure, some positional isomers of the supported $(\eta^5\text{-}C_5Me_5)Rh^{2+}$ group were converted to a

single isomer. [2] The red solution was allowed to cool to room temperature and then filtered through a folded filter paper (Whatman No. 2) into a 1 l beaker (black by-products were removed). To the stirred clear-red filtrate, about 1 l of ethyl acetate was added in small portions. At first a red powder reprecipitated, and then a fine yellow powder deposited. This suspension was stirred in an ice bath for 1 h. The yellow-brown powder was collected on a fine glass frit, washed with ether (5 × 40 ml) and dried overnight under vacuum. (The contaminating $NaBF_4$ can be removed because $NaBF_4$ is soluble in excess ethyl acetate.) Yield: 0.33 g (21%) of yellow-brown powder which is soluble in DMSO but insoluble in CH_3CN, ether and ethyl acetate (see footnote 2). This compound is soluble in water with color change of yellow-brown to yellow-orange. The ^1H NMR spectrum in D_2O showed a very broad signal around 1.76 ppm due to the methyl group.
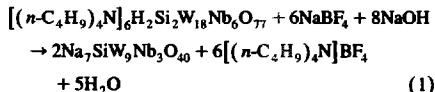
2.4.1. Microanalysis

The sample was dried overnight at room temperature under reduced pressure (ca. 10^{-3} to 10^{-4} Torr) before analysis. Found: C, 5.71; H, 1.11; Na, 3.67; Nb, 8.61; O, 21.0; Rh, 2.60; S, 2.65; Si, 1.22; W, 51.3; total: 97.9%. Calc. for $H_{37}C_{16}Na_5SiW_9Nb_3RhO_{45}S_3$: C, 5.96; H, 1.16; Na, 3.56; Nb, 8.64; O, 22.3; Rh, 3.19; S, 2.98; Si, 0.87; W, 51.3%. TG/DTA: weight loss of 6.2% below 200 °C with a small endothermic point at 55 °C and of 5.9% above 200 °C with the decomposition at 289 °C. Calc. for $Na_7[(\eta^5\text{-}C_5Me_5)Rh \cdot SiW_9Nb_3O_{40}] \cdot 3Me_2SO \cdot 2H_2O$, 1.1% ($2H_2O$) and 7.3% (3DMSO). IR (KBr), (Fig. 2(b)): 1465–1384, 958, 920, 884, 795 cm^{-1}. ^{183}W NMR (DMSO-d_6, 295 K), (Fig. 3(b)): δ −52.7 (2W, $\Delta\nu_{1/2}$ = 5.9 Hz); −90.6 (2W, $\Delta\nu_{1/2}$ = 6.9 Hz); −103.0 (2W, $\Delta\nu_{1/2}$ = 5.7 Hz); −148.6 (2W, $\Delta\nu_{1/2}$ = 6.8 Hz); −152.8 (1W, $\Delta\nu_{1/2}$ = 6.6 Hz). ^1H NMR (DMSO-d_6, 295 K): δ 1.76 (C_5Me_5, s). ^{13}C NMR (DMSO-d_6, 295 K): δ 8.36 (C_5Me_5, s); 92.6 (C_5Me_5, s); 40.4 (Me_2SO, s).

3. Results and discussion

The heptasodium salt (1) of the Keggin-type heteropolyoxoanion $SiW_9Nb_3O_{40}^{7-}$ has been prepared from the organic solvent-soluble, dimeric precursor [(n-C_4H_9)$_4$N]$_6H_2Si_2W_{18}Nb_6O_{77}$, in which two monomeric

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[2] The yield of the mixture with positional isomers, but without $NaBF_4$, was 0.52g (33%), the sample of which has been obtained directly by two reprecipitations by ethyl acetate from the DMSO solution without the second work-up of heating at 84 °C for 3 h in dry DMSO solution. Thus, the yield of the single isomer from the mixture with the positional isomers was 63%.

Keggin units are coupled through three Nb–O–Nb bonds [10–12] as shown in Eq. (1).

$$\left[(n\text{-}C_4H_9)_4N\right]_6H_2Si_2W_{18}Nb_6O_{77} + 6NaBF_4 + 8NaOH$$
$$\rightarrow 2Na_7SiW_9Nb_3O_{40} + 6\left[(n\text{-}C_4H_9)_4N\right]BF_4$$
$$+ 5H_2O \qquad (1)$$

It is isolated as its water-soluble, analytically pure sodium salt on up to an 11.3 g scale (61% yield of a white solid). Key points in the synthesis of $Na_7SiW_9Nb_3O_{40}$ are as follows: (a) the use of stoichiometric amounts (6 equivalents) of $NaBF_4$ to allow for exchange of the $[(n\text{-}C_4H_9)_4N]^+$ countercations of the dimeric, organic solvent-soluble precursor, $[(n\text{-}C_4H_9)_4N]_6H_2Si_2W_{18}Nb_6O_{77}$; (b) the use of a total of 8 equivalents of NaOH to react with the two protons in the dimer (requiring 2 equivalents of OH^-) and to hydrolytically cleave the bridging Nb–O–Nb bond (requiring an additional 6 equivalents of OH^- and forming $5H_2O$); (c) the removal of $[(n\text{-}C_4H_9)_4N]BF_4$ from the reaction mixture and purification to an analytically pure white solid by repeated reprecipitation from an aqueous pH 8 unbuffered solution by the addition of excess CH_3CN.
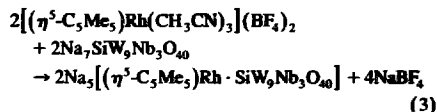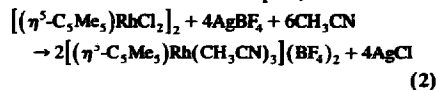
The molecular formula of 1 is established by an elemental analysis (all elements, including oxygen, 98.5% total observed; see the Section 2.3). TG analysis with a temperature ramp of 1 °C min^{-1} shows the presence of $16H_2O$, in accord with the findings of the elemental analysis. Two full elemental analyses of the same compound were carried out: one at room temperature as it was and the other for the sample dried overnight at room temperature under reduced pressure (10^{-3} to 10^{-4} Torr); these show the former sample with 16 hydrates and the latter with four hydrates. We have handled the sample with 16 hydrates under atmospheric conditions without noticeable problems.

The solid FT-IR spectra, measured as KBr disks, of $Na_7SiW_9Nb_3O_{40} \cdot 16H_2O$ obtained here (Fig. 2(a)) and of $(Bu_4N)_7SiW_9Nb_3O_{40}$ (Fig. 2(c)) separately prepared according to Ref. [11], are completely coincident, except for the typical vibrational bands due to the Bu_4N^+ countercations observed in the 1485–1380 cm^{-1} region which are of course absent in the all-Na$^+$ salt. In these spectra, the characteristic and intense 690 cm^{-1} band, due to the vibration of three bridging Nb–O–Nb linkages present in the dimeric polyoxoanion $Si_2W_{18}Nb_6O_{77}^{8-}$ [11], disappears. Infrared measurements (Fig. 2(a) and Fig. 2(c)) confirm that the Keggin-type "$SiW_{12}O_{40}^{-}$" heteropolytungstate framework remains intact under the conditions of the synthesis [17].

Further solution characterization relied on ^{183}W NMR. The ^{183}W NMR spectrum of $Na_7SiW_9Nb_3O_{40}$ in D_2O (Fig. 3(a)) shows primarily two peaks at -121.2 and -127.3 ppm with integrated intensities 2:1. The integrated intensities are in accord with the presence of

a tungsten belt consisting of six WO_6 octahedra and a tungsten cap of three WO_6 octahedra, as expected for a Keggin heteropolyanion (Fig. 1(A)).

The pentasodium salt, $Na_5[(\eta^5\text{-}C_5Me_5)Rh \cdot SiW_9Nb_3O_{40}]$ (2), in which $(\eta^5\text{-}C_5Me_5)Rh^{2+}$ is supported on the Keggin-type heteropolyoxoanion $SiW_9Nb_3O_{40}^{7-}$, has been synthesized according to Eq. (2) and (3). Reaction of $Na_7SiW_9Nb_3O_{40}$ with $(\eta^5\text{-}C_5Me_5)Rh^{2+}$ in a solvent mixture of DMSO–CH_3CN (volume ratio 7.2 ml:34 ml) afforded the target compound on a 0.33 g scale (yield: 21%) as a yellow-brown solid. (We also, unsuccessfully, tried to prepare the target compound by heating $(TBA)_5[(\eta^5\text{-}C_5Me_5)Rh \cdot SiW_9Nb_3O_{40}]$ with 5 equivalents of $NaBF_4$ in dry CH_3CN under reflux. This route failed since, during the course of the reaction, a precipitate forms which is a mixture of the $TBA_{5-x}Na_x$ salt. No further characterization of this material was attempted.)

$$\left[(\eta^5\text{-}C_5Me_5)RhCl_2\right]_2 + 4AgBF_4 + 6CH_3CN$$
$$\rightarrow 2\left[(\eta^5\text{-}C_5Me_5)Rh(CH_3CN)_3\right](BF_4)_2 + 4AgCl$$
$$(2)$$

$$2\left[(\eta^5\text{-}C_5Me_5)Rh(CH_3CN)_3\right](BF_4)_2$$
$$+ 2Na_7SiW_9Nb_3O_{40}$$
$$\rightarrow 2Na_5\left[(\eta^5\text{-}C_5Me_5)Rh \cdot SiW_9Nb_3O_{40}\right] + 4NaBF_4$$
$$(3)$$

This compound is fully soluble in dry DMSO, insoluble in CH_3CN and EtOAc, but soluble in water with color change of yellow-brown to yellow-orange (see the Section 2.4).

The choice of DMSO–CH_3CN as the solvent mixture has proven crucial for the successful synthesis of 2. This follows from the following solubility and stability properties of the two main reagents: the $Na_7SiW_9Nb_3O_{40}$ starting material (see Eq. (3)) is soluble in water and DMSO, but insoluble in CH_3CN; the second reactant itself, $[(\eta^5\text{-}C_5Me_5)Rh(solvent)_3]^{2+}$, is much more stable in solutions of CH_3CN or DMSO than in water. Notably, the use of a single solvent did not allow the reaction described in Eq. (3) to be carried out successfully: (a) in CH_3CN, the reaction did not proceed quantitatively, even with heating under reflux; (b) in water, no reaction was observed; (c) in DMSO, on mixing with $SiW_9Nb_3O_{40}^{7-}$, decomposition of $[(\eta^5\text{-}C_5Me_5)Rh]^{2+}$ took place as judged by its immediate color change to brown and further color change to black with heating. These initial observations suggested the use of a mixed solvent system, specifically DMSO and CH_3CN.

The reaction conditions were then further optimized by monitoring the reaction progress by FT-IR and ^{1}H NMR spectroscopy [2]. It was found that the reaction was sensitive to a number of experimental parameters. Specifically, these are: (a) the order of addition of the

Table 2
Comparison of the chemical shifts (^{183}W NMR) reported for $Na_7SiW_9Nb_3O_{40}$, $Na_5[(\eta^5-C_5Me_5)Rh \cdot SiW_9Nb_3O_{40}]$ and $(Bu_4N)_5[(\eta^5-C_5Me_5)Rh \cdot SiW_9Nb_3O_{40}]$

Complex	δ (D$_2$O)	δ (DMSO-d_6)
$Na_7SiW_9Nb_3O_{40}$ [a]	-121.2; -127.3	—
$Na_5[(\eta^5-C_5Me_5)Rh \cdot SiW_9Nb_3O_{40}]$ [a]	—	-52.7; -90.6; -103.0; -148.6; -152.8
$(Bu_4N)_5[(\eta^5-C_5Me_5)Rh \cdot SiW_9Nb_3O_{40}]$ [b]	—	-50.7; -90.8; -102.8; -148.3; -152.8

[a] This work. [b] Ref. [11].

organic solvents, that is, initially 24 ml CH$_3$CN and *then* 7.2 ml DMSO; (b) the *exact* ratio of DMSO vs. $[(\eta^5-C_5Me_5)RhCl_2]_2$ and the polyoxoanion-support; (c) the *exact* ratio of CH$_3$CN vs. DMSO (total 34 ml vs. 7.2 ml); (d) two work-ups consisting of heating at 84 °C (the first for 4 h in the mixed DMSO–CH$_3$CN media for the synthetic reaction (Eq. (3)), and the second for 3 h only in dry DMSO to prepare a single species from the positional isomers of the supported (η^5-C$_5$Me$_5$)Rh^{2+} group) (see footnote 2). In fact, ^{1}H NMR (Table 1) shows that both work-up steps are required. It is noteworthy that the requisite (d) for the preparation of **2** is quite different from that of only one heating step in the mixed DMSO–CH$_3$CN media carried out for the preparation of the Dawson-type analog, Na$_7$[(η^5-C$_5$Me$_5$)Rh · P$_2$W$_{15}$Nb$_3$O$_{62}$] [2]. These differences, compared with the solubility and stability of Na$_7$[(η^5-C$_5$Me$_5$)Rh · P$_2$W$_{15}$Nb$_3$O$_{62}$] [2], are probably attributed to the higher solubility of **2** in dry DMSO, but the lower stability of **2** in DMSO containing the waters of hydration from the starting material **1**. Regardless of the exact explanation, the small amount of added DMSO acts as a cosolvent and aids in solubilizing the starting materials **1** in the main reaction medium CH$_3$CN.

The molecular formula of **2** is established by an elemental analysis (all elements, including oxygen, 97.9% total observed; see the Section 2.4). Given the absence of any other sources of sulfur, the S analysis (calc. 2.98, found 2.65%) reflects the presence of solvated DMSO. The additional evidence for the presence of solvated DMSO is provided by ^{13}C NMR in DMSO-d_6 as a single peak at 40.4 ppm due to two methyl carbons. TG analyses with a temperature ramp of 1 °C min^{-1} confirm the presence of solvated DMSO and suggest the presence of hydrated waters (total observed weight loss 12.10% below 289 °C).

The infrared measurements (Fig. 2(b)) also confirm that the Keggin-type, "SiM$_{12}$O$_{40}^{n-}$" heteropolytungstate framework remains intact under the conditions of synthesis [17]. Interestingly, the IR spectrum (KBr disk) shows very weak and broad bands consisting of a number of weak peaks between 1465–1384 cm^{-1}. These weak bands are attributed to the presence of the supported (η^5-C$_5$Me$_5$)Rh^{2+} organometallic moiety, and are the first such observation in the Keggin-type polyoxoanions. Such very weak and broad bands due to

C–H vibrations of the supported (η^5-C$_5$Me$_5$)Rh^{2+} group have also been observed in the all-sodium salt of the Dawson-type analog [2]. They could not be observed in the all-Bu$_4$N$^+$ (Fig. 2(d)) or mixed Bu$_4$N$^+$–Na$^+$ salts of [(η^5-C$_5$Me$_5$)Rh · SiW$_9$Nb$_3$O$_{40}$]$^{5-}$, owing to the presence of very intense vibrational bands characteristic of Bu$_4$N$^+$ (1486–1381 cm^{-1}) [11].

Further solution characterization relied on ^{1}H, ^{13}C and ^{183}W NMR spectroscopies (Tables 1 and 2). ^{1}H and ^{13}C NMR spectra (Table 1) in DMSO-d_6 all confirm the existence of only a single species of Na$_5$[(η^5-C$_5$Me$_5$)Rh · SiW$_9$Nb$_3$O$_{40}$] in solution (see footnote 2). The ^{1}H NMR spectrum exhibits one resonance at 1.76 ppm that is assigned to the methyl protons of the η^5-C$_5$Me$_5$ ligand. The ^{13}C NMR spectrum shows two peaks at 8.36 and 92.6 ppm due to the methyl and the ring carbons of the η^5-C$_5$Me$_5$ group respectively.

The ^{183}W NMR spectrum of Na$_5$[(η^5-C$_5$Me$_5$)Rh · SiW$_9$Nb$_3$O$_{40}$] in DMSO-d_6 (Fig. 3(b)) shows five peaks at -52.7, -90.6, -103.0, -148.6 and -152.8 ppm with integrated intensities of 2:2:2:2:1. This spectral pattern is in accord with those of the previously reported all-Bu$_4$N$^+$ and/or mixed Bu$_4$N$^+$–Na$^+$ salts [10,11]. The five-line ^{183}W NMR spectrum also requires that the supported complex has an overall C_s symmetry on the ^{183}W NMR time scale (Fig. 3(b)).

4. Conclusion

The syntheses and isolations of the water-soluble, all-sodium salts of the Keggin-type heteropolyanions, Na$_7$SiW$_9$Nb$_3$O$_{40}$ · 16H$_2$O (**1**) in 61% yield on an 11.3 g scale, and Na$_5$[(η^5-C$_5$Me$_5$)Rh · SiW$_9$Nb$_3$O$_{40}$] · 3DMSO · 2H$_2$O (**2**) in 21% yield on a 0.33 g scale, are described. **1** and **2** have been unequivocally characterized, both in solution and in the solid state. The synthetic procedure for **2** includes much more sophisticated work-ups than those of the all-Bu$_4$N$^+$ and the mixed Bu$_4$N$^+$–Na$^+$ salts, yet simultaneously complements the previously reported syntheses of the latter. This procedure also provides a rare series of identical polyoxoanion-supported complexes with a varied countercation composition. Owing to the decisive influence that the countercation composition has on solubility and other properties, this in turn allows for a systematic study of

the physical properties and reactivity over a range of widely differing solvents and different countercation compositions. In addition, the crystalline $SiW_9Nb_3O_{40}^{7-}$ is also of interest as a possible new type of solid-base catalyst [18].

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