

The all-sodium salt of a polyoxoanion-supported organometallic complex: synthesis and characterization of $\text{Na}_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}] \cdot 7\text{DMSO} \cdot 5\text{H}_2\text{O}$

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Abstract

The preparation of $\text{Na}_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$, a Dawson-type polyoxoanion-supported organometallic complex with all-inorganic counteranions, is described. The compound was obtained in 39% yield as an analytically pure, homogeneous yellow–orange solid by a reaction of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CH}_3\text{CN})_3]^{2+}$ with $\text{Na}_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ in a solvent mixture of CH_3CN –DMSO. Compositional characterization was accomplished by a complete elemental analysis, TG–DTA and GLC measurements. Structural characterization in solution was achieved by a combination of ^1H , ^{13}C , ^{31}P and ^{183}W NMR spectroscopy.

Keywords: Rhodium; Sodium; Niobium; Tungsten; Polyoxometallate; Nuclear magnetic resonance

1. Introduction

Recently, we reported the synthesis of the nona-sodium salt of the triniobium-substituted polyoxoanion $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ [1a]. That work was aimed at providing a water-soluble form of the important $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ polyoxoanion (Fig. 1); prior to that work, the $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ polyoxoanion had been available only as its organic solvent-soluble (and water-insoluble) all-TBA⁺ salt (TBA = $[(\text{n-C}_4\text{H}_9)_4\text{N}]^+$) [1b]. Hence, the all-sodium salt of $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ extended the well-documented organometallic chemistry of $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ into aqueous media [1d].

In a separate account, the full details of the synthesis and isolation of polyoxoanion-supported organometallic complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{7-}$ as its all-TBA⁺ salt have been reported [1]. In this compound, the organometallic moiety, $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}]^{2+}$, is bonded to three bridging Nb_2O oxygens that cap the $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ Dawson-type polyoxoanion as shown by a single-crystal X-ray diffraction analysis (Fig. 2). This

complex is soluble in organic solvents (e.g. CH_3CN , DMSO and acetone) but insoluble in water.

The goal of the present work was to extend the concept of water solubility and all-inorganic composition to $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{7-}$. Reasons for the synthesis of an all-sodium polyoxoanion-supported organometallic complex include: (a) its anticipated water solubility, thereby bringing polyoxoanion-organometallic complexes and their reactivity into water (see above), (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 $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ -supported organometallic catalyst precursors [2]. Furthermore, the synthetic procedure described herein provides for a general route to cation metathesis of polyoxoanion-supported complexes. This allows for considerable flexibility in the design of counteranion composition of such complexes, which in turn provides control over the desired solubility properties.

Herein we report the full details of the synthesis and isolation of the all-sodium salt, $\text{Na}_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}] \cdot 7\text{DMSO} \cdot 5\text{H}_2\text{O}$ (1), in 39% yield (1.06 g scale). Also reported are the compositional characteri-

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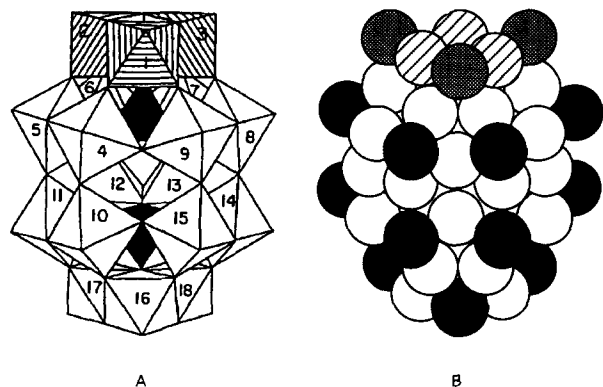


Fig. 1. (A) Polyhedral and (B) space-filling representation of the Dawson-type heteropolyanion α -1,2,3- $P_2W_{15}Nb_3O_{62}^{9-}$. In (A) the three niobiums are represented by hatched octahedra in the 1–3 positions. The WO_6 octahedra occupy the 4–18 positions and two PO_4 groups are shown as the internal, black tetrahedron. In (B) the open circles represent bridging tungsten oxygens (W_2O), while the black circles represent terminal tungsten oxygens (WO). Niobium bridging oxygens (Nb_2O) are depicted by hatched circles, whereas niobium terminal oxygens (NbO) are shown as gray circles. From the space-filling representation it becomes clear that heteropolyoxoanions are composed of a close-packed array of oxygens, and this representation in turn reveals their potential as soluble metal oxide analogs.

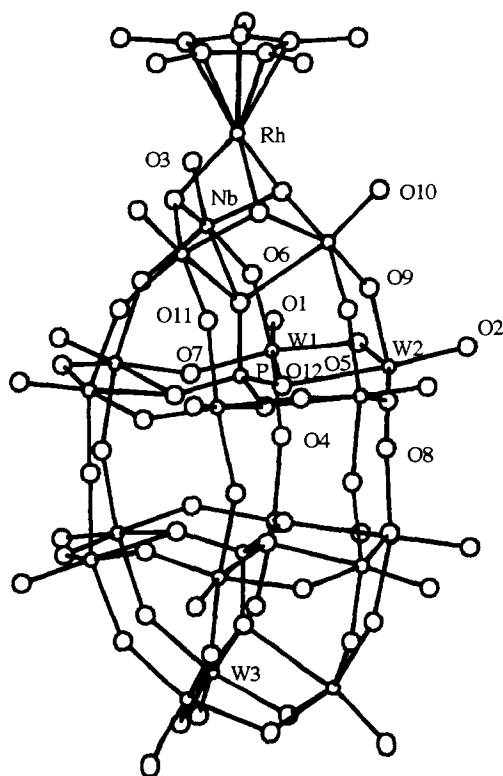


Fig. 2. Structure of $[(C_5Me_5)Rh \cdot P_2W_{15}Nb_3O_{62}]^{7-}$ [1e]. The Nb and W3 atoms each are composite, $Nb_{0.5}W_{0.5}$, because the anion adopts two equally weighted orientations related by the mirror plane of a $3/m$ (D_{3h}) crystallographic site. The C_5Me_5 group lies in a plane normal to the anion C_3 axis, and is disordered because of the incompatibility of its fivefold symmetry with that axis. The C_5Me_5 could not be located by X-ray single-crystal structure analysis but is present by 1H NMR spectroscopy and elemental analysis.

zation of **1** by a full elemental analysis, FT-IR, thermogravimetric and differential thermal analyses (TG/DTA) and GLC and the structural characterization of **1** in solution by 1H , ^{13}C , ^{31}P and ^{183}W NMR spectroscopy.

2. Experimental details

2.1. General conditions

The followings were used as received: $AgBF_4$, CH_3CN , DMSO, EtOAc, Et_2O , 3A molecular sieves (all from Wako) and $DMSO-d_6$ (Aldrich). $[(\eta^5-C_5Me_5)RhCl_2]_2$ [1b,3a,b] and $Na_9P_2W_{15}Nb_3O_{62} \cdot 23H_2O$ [1a] were prepared according to the literature.

2.2. Instrumentation and analytical procedures

Elemental analyses were carried out by Mikroanalytisches Labor Pascher (Remagen, Germany). Infrared spectra were recorded on a Nicolet 510 FT-IR spectrometer in KBr disks at room temperature.

TG and DTA were carried out using a Seiko SSC 5000 TG/DTA 300 system. TG/DTA measurements were run under air with a temperature ramp of first $10^\circ C \text{ min}^{-1}$ and then, in separate experiments (for more precise data), $2.5^\circ C \text{ min}^{-1}$ between 20 and $400^\circ C$. GLC measurements were carried out on a Shimadzu GC-8APT instrument which was equipped with an Apiezon grease L column (column length 2 m; column temperature $130^\circ C$). For GLC analyses, 47.2 mg of the heteropolyoxoanion sample was dissolved in 1 ml of dry DMSO and 10 μ l of benzene were added as an internal standard. The solvent DMSO used for the GLC measurements was dried using molecular sieves and the lack of GLC-detectable water in the dried DMSO was confirmed by GLC analysis.

1H NMR (399.65 MHz), ^{13}C NMR (100.40 MHz) and ^{31}P NMR (161.70 MHz) spectra were recorded at $22^\circ C$ in 5 mm o.d. tubes on a JEOL JNM-EX 400 FT-NMR spectrometer with a JEOL EX-400 NMR data processing system. 1H and ^{13}C NMR spectra were referenced to an internal standard of tetramethylsilane (TMS). Chemical shifts are reported on the δ scale and resonances downfield of TMS (δ 0) are recorded as positive. ^{31}P NMR spectra were referenced to an external standard of 25% H_3PO_4 in H_2O in a sealed capillary. Chemical shifts are reported as negative for resonances upfield of H_3PO_4 (δ 0). ^{183}W NMR (16.50 MHz) spectra were recorded at $22^\circ C$ 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 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. Preparation of $\text{Na}_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}] \cdot 7\text{DMSO} \cdot 5\text{H}_2\text{O}$ (1)

Finely ground $\text{Na}_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62} \cdot 23\text{H}_2\text{O}$ (2.50 g, 0.531 mmol) that had been well dried under vacuum overnight was placed in a 100 ml three-necked round-bottomed flask. Next, 40.0 ml of CH_3CN (dried over molecular sieves) and exactly 10.0 ml of DMSO (dried over molecular sieves) were added while stirring with a magnetic stir bar. Using a long needle, dry N_2 was passed through the resulting suspension for 30 min. In a separate beaker, $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2]_2$ (0.164 g; 0.265 mmol) was slurried in 10 ml of dry CH_3CN . Solid AgBF_4 (0.207 g; 1.06 mmol; 4 equiv.) was added to the slurry, causing the immediate formation of an AgCl precipitate. The mixture was stirred for 10 min (magnetic stir bar), and then filtered through a medium glass frit directly into the stirred suspension of $\text{Na}_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$. The precipitate on the glass frit was washed with ca. 5 ml of CH_3CN using a pipette and the washings were also introduced to the heteropolyoxoanion suspension. Upon introduction of the in situ-generated yellow-orange $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CH}_3\text{CN})_3](\text{BF}_4)_2$ solution, the color of the heteropolytungstate changed from white to yellow–orange. The resulting suspension was stirred under a stream of N_2 (with the N_2 inlet needle being above the solution) at 85°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. 50 ml of CH_3CN , then washed three times with ca. 50 ml of diethyl ether and dried under vacuum overnight. (The yield at this stage of the preparation was typically 2.6 g. The material is a mixture of $\text{Na}_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$ and NaBF_4 .) Next, the dry material was transferred into a beaker and ca. 5 ml of DMSO were added. The resulting cloudy orange solution was filtered through a folded filter-paper (Whatman No. 2) into a 1 l beaker. To the stirred clear-orange filtrate, about 500 ml of ethyl acetate were added in small portions. First red powder reprecipitated, then fine yellow powder was deposited. This suspension was stirred for 30 min while cooling with an ice–water bath. The now yellow–orange powder was collected on a fine glass frit, washed with diethyl ether (3×50 ml) and dried overnight under vacuum. To remove completely the contaminating NaBF_4 , the reprecipitation described above was repeated three more times. Yield: 1.06 g (39%) of yellow–orange powder, which is soluble in DMSO but insoluble in diethyl ether, acetonitrile and ethyl acetate.

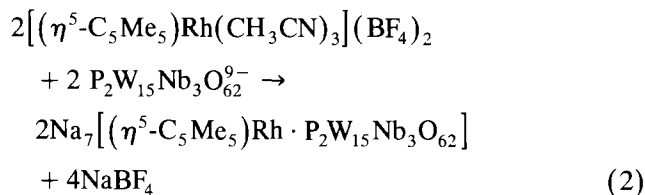
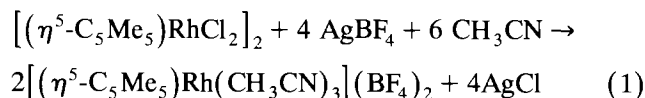
Microanalysis. Found: H, 1.65; C, 5.31; Na, 3.20; P, 1.16; W, 53.6; Nb, 5.24; Rh, 1.84; O, 23.5; S, 4.09%;

total, 99.59%. $\text{H}_{67}\text{C}_{24}\text{Na}_7\text{P}_2\text{W}_{15}\text{Nb}_3\text{RhO}_{74}\text{S}_7$ calc.: H, 1.32; C, 5.62; Na, 3.14; P, 1.21; W, 53.8; Nb, 5.44; Rh, 2.01; O, 23.1; S, 4.38%. The additional evidence for the presence of water of solvation comes from GLC measurements in DMSO solution. GLC analysis: solvated water ($x\text{H}_2\text{O}$), found: 1.7 ± 0.1 wt%; calc. 1.76% for $x = 5$. TG/DTA: weight loss of 7.47% below 87.5°C and 7.03% between 87.5 and 300°C (at $2.5^\circ\text{C min}^{-1}$; total 14.5%) with a sharp endothermic point at 41.2°C ; Calc. for $\text{Na}_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}] \cdot 7\text{Me}_2\text{SO} \cdot 5\text{H}_2\text{O}$, 1.76% ($5\text{H}_2\text{O}$) and 10.67% (7DMSO). IR (KBr) (Fig. 3(a)): ν 1466w, 1459w, 1438w, 1419w, 1405w, 1384w, 1122w, 1087s, 1059w, 1017m, 946s, 915s, 777s, 532m cm^{-1} . ^{31}P NMR (DMSO- d_6 , 301 K, ca. 50 mM) (Fig. 4): δ -8.3 (1.0 P, $\Delta\nu_{1/2} = 5.6 \pm 0.6$ Hz); -14.0 (1.0 P, $\Delta\nu_{1/2} = 5.6 \pm 0.6$ Hz). ^{183}W NMR (DMSO- d_6 , 296 K, ca. 39 mM) (Fig. 5): δ -133.4 (3W, $\Delta\nu_{1/2} = 7.1 \pm 0.2$ Hz); -154.3 (6W, $\Delta\nu_{1/2} = 7.0 \pm 0.2$ Hz); -188.2 (6W, $\Delta\nu_{1/2} = 5.3 \pm 0.2$ Hz). ^1H NMR (DMSO- d_6 , 302 K, ca. 50 mM): δ 1.84 (C_5Me_5 , s). ^{13}C NMR (DMSO- d_6 , 303 K, ca. 46 mM): δ 8.5 (C_5Me_5 , s); 93.6 (C_5Me_5 , s); 40.4 (Me_2SO , s).

In water (D_2O), decomposition occurs as judged by ^{31}P NMR (1 in D_2O shows the two resonances at -7.7 and -14.2 ppm characteristic of free $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$).

3. Results and discussion

The hepta sodium salt $\text{Na}_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$ (1), in which $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}^{2+}$ is supported on the Dawson-type heteropolyoxoanion $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$, was synthesized according to Eqs. (1) and (2). Reaction of $\text{Na}_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ and $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}^{2+}$ in a solvent mixture of DMSO– CH_3CN (1:5, v/v) afforded the target compound on a 1.06 scale (yield: 39%) as a yellow–orange solid [4].



This compound is fully soluble in dry DMSO, but insoluble in CH_3CN and EtOAc . In water, decomposition occurs and the organometallic moiety, $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}^{2+}$, is cleaved off the heteropolyoxoanion support (as evidenced by a ^{31}P NMR spectrum of 1 in D_2O ; see the Experimental section).

The choice of DMSO– CH_3CN as the solvent mixture proved crucial for the successful synthesis of 1. This follows from the following solubility and stability

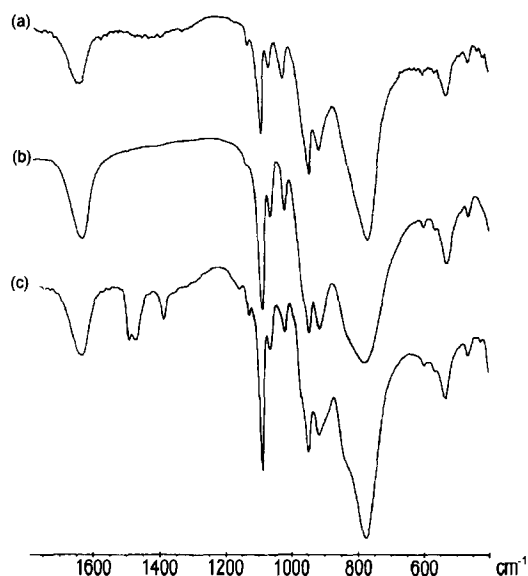


Fig. 3. FT-IR spectra, measured in KBr disks, of (a) $\text{Na}_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}] \cdot 7\text{DMSO} \cdot 5\text{H}_2\text{O}$, (b) $\text{Na}_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62} \cdot 23\text{H}_2\text{O}$ and (c) $(\text{TBA})_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}] \cdot 3\text{CH}_3\text{CN}$. The observation of the characteristic Dawson-type polyoxoanion IR bands between 1100 and 700 cm^{-1} demonstrates that the $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ support ion remains intact under the conditions of the synthesis [5]. In spectrum (a), many weak peaks are observable between 1465 and 1384 cm^{-1} ; these are attributed to the vibrations of the supported $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}^{2+}$ moiety. In contrast, these bands are obscured in (c) by the very intense C–H vibrations of the TBA^+ counteranions.

properties of the two main reagents: the $\text{Na}_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$ starting material (cf. Eq. (1)) is soluble in water and DMSO, but insoluble in CH_3CN ; the second reactant, $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{solvent})_3]^{2+}$, 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. (2) to be carried out successfully: (a) in acetonitrile, the reaction did not proceed quantitatively, even with heating under reflux, (b) in water, no reaction was observed, and (c) in DMSO, decomposition of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}]^{2+}$ took place as judged by its immedi-

ate color change to brown on mixing with $\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}^{9-}$ and further color change to black with heating. These initial observations suggested the use of a mixed solvent system comprising DMSO and CH_3CN .

The reaction conditions were then further optimized by monitoring the reaction progress by ^{31}P NMR spectroscopy. It was found that the reaction is sensitive to a number of experimental parameters. Specifically, these are: (a) the order of addition of the organic solvents, that is, initially CH_3CN and then DMSO, (b) the exact ratio of DMSO to $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2]_2$ and the polyoxoanion support, (c) the exact ratio of CH_3CN to DMSO and (d) a relatively long reaction time of 4 h at 85°C. Apparently, the small amount of added DMSO acts as a co-solvent and aids in solubilizing the starting material, $\text{Na}_9\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}$, in the reaction medium CH_3CN .

The molecular formula of **1** is established by an elemental analysis (all elements, including oxygen, 99.6% total observed; see Experimental section). In the absence of any other sources of sulfur, the S analysis (Calc. 4.38, found 4.09%) 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. Thermogravimetric analyses with two different temperature ramps of 2.5°C min^{-1} and, in a separate experiment, 10.0°C min^{-1} confirm the presence of solvated DMSO and suggest the presence of hydrated waters (total observed weight loss 14.50% and 14.34%, respectively). Additional evidence for the presence of solvate water came from GLC measurements of **1** (see Experimental section for details).

Infrared measurements (Fig. 3(a)) confirm that the Dawson-type, “ $\text{P}_2\text{M}_{18}\text{O}_{62}^{n-}$ ” heteropolytungstate framework remains intact under the conditions of synthesis [5].

Interestingly, the IR spectrum (KBr disc) shows a number of weak bands between 1465 and 1384 cm^{-1} (in addition to the vibrational bands typical of a Dawson-type polyoxoanion framework). These weak bands

Table 1

Comparison of the chemical shifts (^{31}P and ^{183}W NMR) reported for $\text{Na}_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$, $\text{Na}_9[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$ and $(\text{Bu}_4\text{N})_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$

| ^{31}P NMR | δ (D_2O) | δ (CD_3CN) | δ ($\text{DMSO}-d_6$) |
|--|-----------------------------------|-------------------------------------|--------------------------------|
| $\text{Na}_9[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}] \cdot 23\text{H}_2\text{O}$ ^a | –7.7; –14.2 | – | –7.6; –14.1 |
| $\text{Na}_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}] \cdot 7\text{DMSO} \cdot 5\text{H}_2\text{O}$ ^b | – | – | –8.3; –14.0 |
| $(\text{Bu}_4\text{N})_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}] \cdot 3\text{CH}_3\text{CN}$ ^c | – | –8.2; –13.9 | –8.5; –14.2 |
| ^{183}W NMR | δ (D_2O) | δ ($\text{DMSO}-d_6$) | |
| $\text{Na}_9[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}] \cdot 23\text{H}_2\text{O}$ ^a | –151.6; –177.2; –219.8 | 137.4; 163.5; –206.9 | |
| $\text{Na}_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}] \cdot 7\text{DMSO} \cdot 5\text{H}_2\text{O}$ ^b | – | –133.4; –154.3; –188.2 | |
| $(\text{Bu}_4\text{N})_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}] \cdot 3\text{CH}_3\text{CN}$ ^c | – | –130.6; –153.0; –185.5 | |

^a Ref. [1a].

^b This work.

^c Ref. [1e].

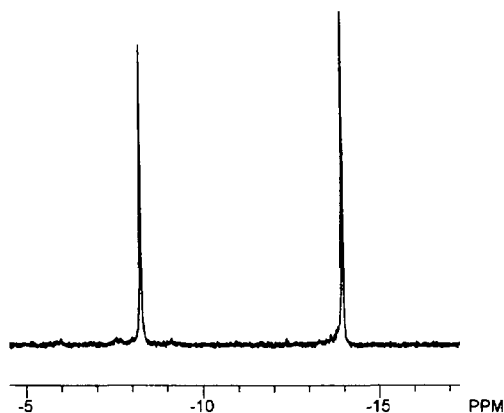


Fig. 4. ^{31}P NMR spectrum of $\text{Na}_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$ in $\text{DMSO-}d_6$ showing a high homogeneity and purity ($\geq 95\%$) for the polyoxoanion-supported organometallic $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}]^{2+}$.

are attributed to the presence of the supported $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}^{2+}$ organometallic moiety. They could not be observed in the mixed $\text{Bu}_4\text{N}^+\text{-Na}^+$ salts of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{7-}$, owing to the presence of very intense vibrational bands characteristic of Bu_4N^+ ($1486\text{--}1381\text{ cm}^{-1}$) [1e].

Further solution characterization relied on ^1H , ^{13}C , ^{31}P and ^{183}W NMR spectroscopy (Table 1). ^1H , ^{13}C and ^{31}P NMR spectra in $\text{DMSO-}d_6$ all confirm the existence of only a single species of $\text{Na}_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$ in solution. The ^1H NMR spectrum exhibits one resonance at 1.84 ppm that is assigned to the methyl protons of the $\eta^5\text{-C}_5\text{Me}_5$ ligand. The ^{13}C NMR spectrum shows two peaks at 8.5 and 93.6 ppm due to the methyl and the ring carbons of the $\eta^5\text{-C}_5\text{Me}_5$ group, respectively. Finally, the clean two-line ^{31}P NMR spectrum of **1** demonstrates that only a single heteropolyanion species is present in solution with the downfield resonance at -8.3 ppm assigned to the phosphorus closest to the Nb_3O_6 site, whereas the upfield resonance at -14.0 ppm is attributed to the phosphorus

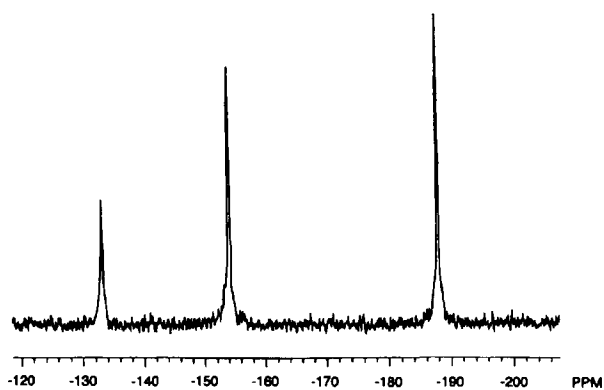


Fig. 5. ^{183}W NMR spectrum of $\text{Na}_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$ in $\text{DMSO-}d_6$. The observed three-line spectrum shows that the complex has C_{3v} (pseudo) symmetry on the ^{183}W NMR time-scale.

closer to the W_3O_6 cap, as discussed previously [1a,b,e] (Fig. 4).

The ^{183}W NMR spectrum of $\text{Na}_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$ in $\text{DMSO-}d_6$ (Fig. 5) shows three peaks at -133.4 , -154.3 and -188.2 ppm with integrated intensities of 1:2:2. This spectral pattern is in accord with the presence of two tungsten belts consisting of six WO_6 octahedra each and a tungsten cap of three WO_6 octahedra [1a,b,e], as is expected for a Wells–Dawson heteropolyoxoanion. The three-line ^{183}W NMR spectrum also requires that the supported complex has overall C_{3v} symmetry of the ^{183}W NMR time-scale (Fig. 5).

4. Conclusion

The synthesis and isolation of $\text{Na}_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}] \cdot 7\text{DMSO} \cdot 5\text{H}_2\text{O}$ in 39% yield and on a 1.06 g scale has been described. This procedure complements the previously reported syntheses of the all- Bu_4N^+ and the mixed $\text{Bu}_4\text{N}^+\text{-Na}^+$ salts of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh} \cdot \text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{7-}$ and, hence, provides a series of identical complexes with varied counteranion composition. Owing to the decisive influence that the counteranion composition has on solubility and other properties, this in turn allows for a systematic study of physical properties and reactivity over a range of widely differing solvents and different counteranion compositions.

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References and notes

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- [2] The majority of heteropolyoxoanion structures determined by single-crystal X-ray crystallography to date (more than 100 during the last 25 years) have been crystallized from aqueous solution. In contrast, the number of structures reported for organic solvent-soluble heteropolyoxoanions is far less, ca. 20. This situation can in part be attributed to the fact that the development of organic solvent-soluble systems is more recent. More impor-

- tant, however, is the experimental observation that organic solvent-soluble heteropolyoxoanions of higher charge do not readily crystallize, at least (not surprisingly) with “floppy” cations such as $[(n\text{-C}_4\text{H}_9)_4\text{N}]^+$; M. Pohl, *Dissertation*, University of Oregon, 1994.
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- [4] We also, unsuccessfully, tried to prepare the target compound by heating $(\text{TBA})_7[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}\cdot\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]$ with 7 equiv. of NaBF_4 in dry CH_3CN under reflux. This route failed as during the course of the reaction a precipitate forms which is a mixture of the $(\text{Bu}_4\text{N})_{7-x}\text{Na}_x$ salts. No further characterization of this material was attempted.
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