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The Nonasodium Salt of the Triniobium-Substituted Polyoxoanion $P_2W_{15}Nb_3O_{62}^{9-}$: A Water-Soluble, Readily Crystallized Form of This Dawson-Based Soluble Metal–Oxide Organometallics-Support System

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The preparation of the Dawson-type heteropolyoxoanion $P_2W_{15}Nb_3O_{62}^{9-}$ as its water-soluble sodium salt, $Na_9P_2W_{15}Nb_3O_{62}\cdot 23H_2O$, is described. The title compound is obtained on up to a 13-g scale as an analytically pure, homogeneous white solid in 61% yield. It was characterized by a complete elemental analysis, TG/DTA, IR spectroscopy, and multinuclear ^{31}P and ^{183}W NMR spectroscopy.

Introduction

Polyoxoanions are molecular metal-oxide clusters which resemble discrete fragments of solid metal oxides.[2] For this reason, the groups of Klemperer[3] and Finke[4] have exploited these molecular clusters for the support of organometallic fragments such as $Rh(C_5Me_5)^{2+}$, $M(1,5\text{-COD})^+$ (M = Rh, Ir), $M(CO)_3^+$ (M = Mn, Re), $Ti(C_5H_5)^{3+}$, $Ru(C_6H_6)^{2+}$, and other organometallics.[3,4] This work has culminated, recently, in the report of a polyoxoanion-supported catalyst;[5] the necessary mechanistic studies to reveal that the true catalyst is indeed polyoxoanion-supported (under O_2, but not under H_2) have also been completed.[5b,c]

The synthetic strategy in most, but not all,[6] of the work to date has been to make organic solvent-soluble forms of the polyoxoanions, generally via $[(n\text{-}C_4H_9)_4N]^+$ counterions, thereby capitalizing on known organometallic syntheses and chemistry in *organic* solvents such as CH_3CN or CH_2Cl_2, for example. Further advantages of this organic solvent-soluble polyoxoanion approach include the following: the greatly enhanced kinetic stability of polyoxoanions in non-aqueous solvents; the ability to catalyze organic substrate reactions in organic solvents (i.e., without introducing the mechanistic complexities of a two-phase aqueous/organic solvent system); the generally good stability of the organometallic moieties in non-aqueous, organic solvents. *The major disadvantage* of this approach is the fact that $[(n\text{-}C_4H_9)_4N]^+$ salts of polyoxoanions are harder to crystallize. Subsequently, obtaining strongly diffracting crystals needed for X-ray structural determinations is difficult, especially as the charge of the polyoxoanion goes above 2- or 3-.[7] A case in point is that, despite considerable effort, only a single crystal structure of the important, custom-made $P_2W_{15}Nb_3O_{62}^{9-}$ polyoxoanion support system has been described to date, that of $[(C_5Me_5)Rh\cdot P_2W_{15}Nb_3O_{62}]^{7-}$.[8]

It has been realized from the start, however,[4] that an alternative synthetic approach is to exploit the better known water-soluble polyoxoanions (i.e., as their more traditional and readily made M^+ salts; e.g., $M^+ = Li^+, Na^+, K^+, NH_4^+$) and then, instead, bring the *organometallic* chemistry into water. This approach, while perhaps less viable for some catalytic chemistries, is expected to overcome the crystallization problem stated above, since even polyoxoanions as highly charged as 23- have been crystallized from water in a form suitable for single-crystal X-ray diffraction structural determinations.[9] In addition water-soluble organometallics,[10] such as polyoxoanion-supported organometallics, are of current interest in their own right.

A key experimental insight for the present studies came when a single crystal of the all sodium salt, $Na_9P_2W_{15}Nb_3O_{62}$, was obtained from a solution of the mixed $[(n\text{-}C_4H_9)_4N]^+/Na^+$ salt and its structure was solved.[11] This observation suggested to us, as important initial goals of a joint Kanagawa University/

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Colorado State University research effort, the larger scale synthesis and characterization of the all Na^+ salts of the following polyoxoanion support systems and their organometallic derivatives: $P_2W_{15}Nb_3O_{62}^{9-}$,[4g,h] $SiW_9Nb_3O_{40}^{7-}$,[4a,c,j,12] $[(C_5Me_5)Rh{\cdot}P_2W_{15}Nb_3O_{62}]^{7-}$,[4g,8] and $[(C_5Me_5)Rh{\cdot}SiW_9Nb_3O_{40}]^{5-}$.[4a,c,j]

Herein we report success at the first of these goals, the synthesis of the all Na^+ salt, $Na_9P_2W_{15}Nb_3O_{62}{\cdot}23H_2O$ (**1**) in pure form in 61% yield and on up to a 13-g scale, along with its characterization by a full elemental analysis, ^{31}P and ^{183}W NMR, IR, and TGA/DTA methods. Efforts toward the other goals listed above are continuing and will be reported in due course.

Experimental Section

Materials. The following were used as received: $NaBF_4$, 85% H_3PO_4, 0.5 M NaOH aqueous solution, and CH_3CN (all from Wako); $[(n\text{-}C_4H_9)_4N]OH$ (40% aqueous solution) and CD_3CN (Aldrich); D_2O (Merck). $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$ was prepared as previously described.[4g,h]

Instrumentation/Analytical Procedures. Elemental analyses were obtained from Mikroanalytisches Labor Pascher (Remagen, Germany). Infrared spectra were obtained on a Nicolet 510 FT-IR spectrometer as KBr disks at room temperature. Thermogravimetric (TG) and differential thermal analyses (DTA) were acquired using a Seiko SSC 5000 TG/DTA 300. TG/DTA were run under air with a temperature ramp of 10.0 °C/min between 20 and 500 °C.

^{31}P NMR (161.70-MHz) spectra were recorded at 22 °C in 5-mm-o.d. NMR tubes on a JEOL JNM-EX 400 FT-NMR spectrometer and JEOL EX-400 NMR data processing system. ^{31}P NMR were measured both in D_2O and in D_2O adjusted to pD 8.4.[13] Spectra were referenced externally to 8.5% H_3PO_4 in H_2O. Chemical shifts are reported on the δ scale with negative values for resonances upfield of H_3PO_4 (δ 0). Spectral parameters for ^{31}P NMR include the following: pulse width 6.0 μs; acquisition time 0.41 s; repetition rate 1.61 s; sweep width ±20 000 Hz.

^{183}W NMR (16.50-MHz) spectra were recorded at 22 °C in 10-mm-o.d. NMR 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. ^{183}W NMR spectra were measured in D_2O adjusted[13] to pD 8.4 and referenced externally to a saturated Na_2WO_4/D_2O. Chemical shifts are reported on the δ scale with resonances upfield of Na_2WO_4 (δ 0) as negative. Spectral parameters for ^{183}W NMR include the following: pulse width 24.0 μs; acquisition time 1.64 s; repetition rate 2.84 s; sweep width ±2500 Hz. A 0.25-Hz exponential apodization of the FID was applied to all spectra, but was removed from any line widths reported herein.

$Na_9P_2W_{15}Nb_3O_{62}{\cdot}23H_2O$. In a 300-mL beaker were placed 5.00 g (0.451 mmol) of $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$ and 50 mL of CH_3CN. Warming the mixture to 50–60 °C and stirring resulted in a clear solution. While the solution temperature was maintained at 50–60 °C, solid $NaBF_4$ (0.594 g, 5.41 mmol, 12 equiv) was added, followed by stirring for 15 min, during which time all of the $NaBF_4$ dissolved. The resulting pale-yellow solution was allowed to cool to room temperature. Dropwise addition of 5.41 mL (2.71 mmol, 6 equiv) of 0.5 M NaOH resulted in the formation of a mixture of white precipitate and colorless oil. After the addition of base is completed, stirring is continued for an additional 20 min. Purification of the mixture of $Na_9P_2W_{15}Nb_3O_{62}$ and $[(n\text{-}C_4H_9)_4N]BF_4$ was accomplished by repeated reprecipitation with CH_3CN ($[(n\text{-}C_4H_9)_4N]BF_4$ is soluble in CH_3CN whereas the nonasodium heteropolyoxoanion is not). Addition of 50 mL of CH_3CN to the reaction mixture changed all of the white precipitate to a colorless oil. The supernatant, which has been shown by FT-IR spectroscopy to contain both unreacted $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$ and $[(n\text{-}C_4H_9)_4N]BF_4$, was decanted and discarded. The remaining oil at the bottom of the beaker was washed several times with small, 5–10-mL amounts of CH_3CN; the washings were also decanted and discarded. The beaker containing the oily material was then placed in an oven and dried overnight at 55 °C. The typical yield at this stage of the preparation was 3.6 g. Next, up to 30 mL (preferably less) of unbuffered pH 8 water (the pH was adjusted with NaOH) was added, and the residual solid was then redissolved by warming to 60 °C. The warm solution was filtered through a folded filter paper (Whatman No. 2) and the clear filtrate was collected in a 500-mL beaker. To the stirred filtrate, about 450 mL of CH_3CN (i.e., 10–15 times the amount of unbuffered pH 8 water used in dissolving the solid) was added in small portions. Upon addition of acetonitrile, an oil settled at the bottom of the beaker with the supernatant appearing colloidal. For complete sedimentation, the mixture was allowed to stand in a refrigerator for several days. For further workup the colloidal supernatant was removed by decantation, and the remaining mixture of powder and oil was washed several times with small amounts of CH_3CN. Drying overnight at 55 °C yielded 2.6 g (61%) of a white powder. The compound is very soluble in water, but insoluble in acetonitrile. It can be crystallized from a pH 8 unbuffered aqueous solution containing CH_3CN or by vapor diffusion. The synthetic procedure has successfully been scaled-up by a factor of 5, resulting in a 13 g yield and was independently and successfully repeated by one of us (M.P.) at Colorado State.

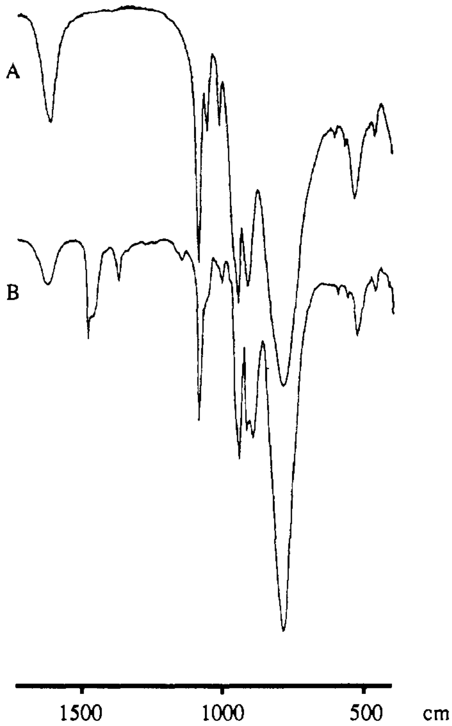

Figure 1. FT-IR spectra, measured as KBr disks, of (A) $Na_9P_2W_{15}Nb_3O_{62}{\cdot}23H_2O$ and of (B) $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ demonstrating that the polyoxoanion region of the IR of these two salts are completely coincident. They do, however, differ as expected in the vibrational bands characteristic of $[(n\text{-}C_4H_9)_4N]^+$ (1380–1485 cm^{-1}). The observation of the characteristic Dawson-type polyoxoanion IR bands between 1100–700 cm^{-1} demonstrate that the "$P_2M_{18}O_{62}^{n-}$" ion remains intact under the conditions of the synthesis.[14]

Anal. Calcd for $H_{46}Na_9P_2W_{15}Nb_3O_{85}$ (found): H, 0.98 (1.01); Na, 4.39 (4.39); P, 1.31 (1.32); W, 58.5 (58.5); Nb, 5.92 (5.92); O, 28.9 (29.1); total, 100.2.

TG/DTA: Weight loss of 8.89% (calculated for 23 hydrated water, 8.79%) below 250 °C, with an endothermic point at 89.5 °C.

IR (KBr disk, cm^{-1}) (Figure 1) (polyoxometalate region): 1087, 1059, 1016, 947, 914, 778, 529. The FT-IR spectra, measured as KBr disks, of $Na_9P_2W_{15}Nb_3O_{62}{\cdot}23H_2O$ (Figure 1A) and $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ (Figure 1B) are completely coincident, with the exception of the vibrational bands characteristic of $[(n\text{-}C_4H_9)_4N]^+$ (1380–1485 cm^{-1}). The characteristic resonances for a Dawson-type heteropolytungstate

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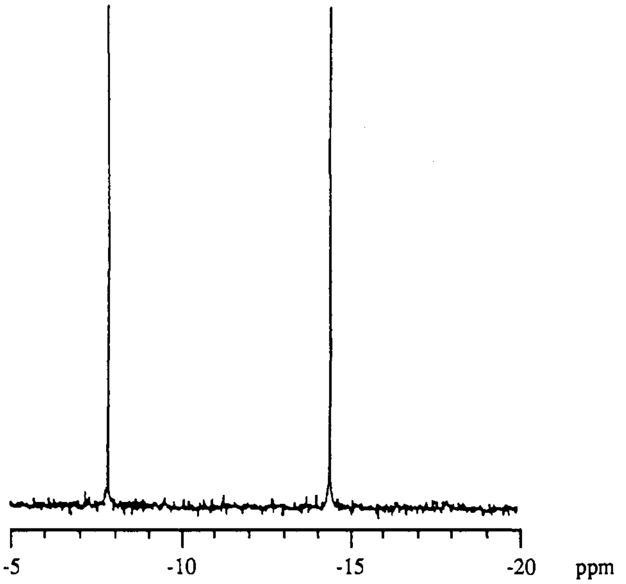

Figure 2. ^{31}P NMR spectrum of $Na_9P_2W_{15}Nb_3O_{62}$ in D_2O. The observed two-line spectrum requires the presence of a single species in solution.

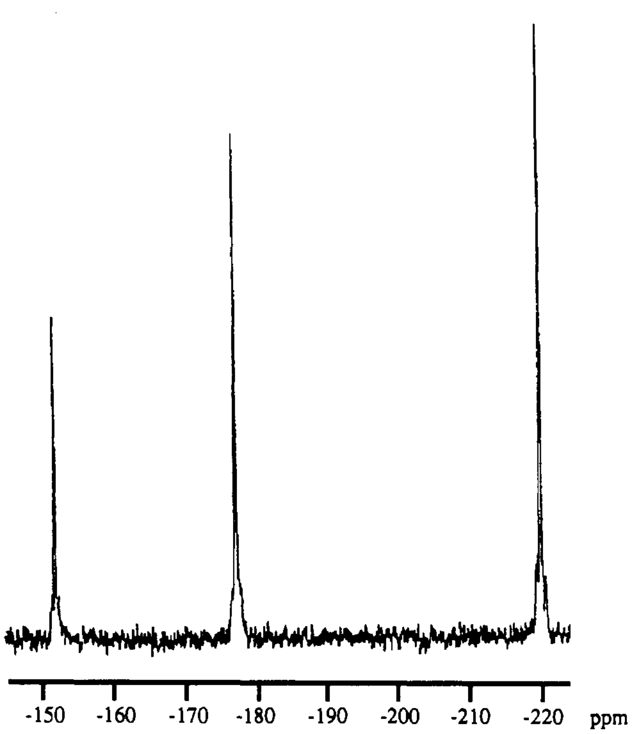

Figure 3. ^{183}W NMR spectrum of $Na_9P_2W_{15}Nb_3O_{62}$ in D_2O adjusted to pD 8.4.[13] The observed three-line spectrum requires the presence of a single C_{3v}-symmetry species in solution.

framework are observed between 1100–700 cm^{-1} and show that the "$P_2M_{18}O_{62}^{n-}$" remains intact under the conditions of the synthesis.[14]

^{31}P (22 °C, 70 mM, D_2O), δ (no. of P, $\Delta\nu_{1/2}$) (Figure 2): −7.8 (1.0 P, 3.8 ± 1.2 Hz), −14.3 (1.0 P, 5.1 ± 1.2 Hz). Spectral pattern, chemical shifts, and half-widths were found to be identical when measured in D_2O which has been adjusted to pD 8.4.[13]

^{183}W (23 °C, 100 mM, D_2O of pH 8.0), δ (no. of W, $\Delta\nu_{1/2}$) (Figure 3): −151.6 (3 W, 3.4 ± 0.3 Hz; $^2J_{W-O-W}$ = 17.1 ± 0.6 Hz), −177.2 (6 W, 4.5 ± 0.3 Hz; $^2J_{W-O-W}$ = 19.8 ± 0.6 Hz), −219.8 (6 W, 3.8 ± 0.3 Hz; $^2J_{W-O-W}$ = 19.5 ± 0.6 Hz).

Results and Discussion

The nonasodium salt of the Dawson-type heteropolyoxoanion $P_2W_{15}Nb_3O_{62}^{9-}$ has been prepared from the organic solvent-soluble, dimeric precursor $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$ as

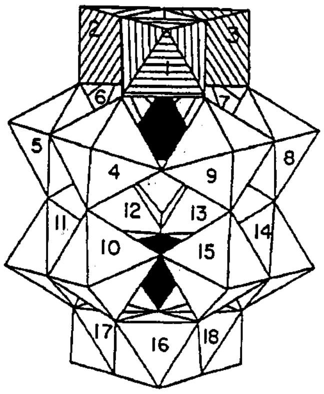

Figure 4. Polyhedral representation of the Dawson-type heteropolyanion α-1,2,3-$P_2W_{15}Nb_3O_{62}^{9-}$. The three niobiums are represented by hatched octahedra in the 1–3 positions. The WO_6 octahedra occupy the 4–18 positions, and the two PO_4 are shown as the two internal, black tetrahedra.

shown in eq 1. It is isolated as its water-soluble, analytically

$$[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123} + 6NaOH + 12NaBF_4 \xrightarrow[\text{2. } CH_3CN \text{ reppt}]{\text{1. } H_2O/CH_3CN} 2Na_9P_2W_{15}Nb_3O_{62}\downarrow + 12[(n\text{-}C_4H_9)_4N]BF_4 + 5H_2O \quad (1)$$

pure sodium salt on up to a 13 g scale (61% yield of a white solid). Key points in the synthesis of $Na_9P_2W_{15}Nb_3O_{62}$ are as follows: (a) the use of stoichiometric amounts (12 equiv) of $NaBF_4$ to allow for exchange of the 12 $[(n\text{-}C_4H_9)_4N]^+$ countercations of the dimeric, organic solvent-soluble precursor, $[(n\text{-}C_4H_9)_4N]_{12}H_4P_4W_{30}Nb_6O_{123}$; (b) the use of a total of 6 equiv of NaOH to react with the four protons in the dimer (requiring 4 equiv of OH^-) and to hydrolytically cleave the bridging Nb–O–Nb bond (requiring an additional 2 equiv of OH^- and forming two H_2O); and (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 aqueous solution by the addition of CH_3CN.

The molecular formula of **1** is established by an elemental analysis (all elements, including oxygen, 100.2% total observed; see Experimental Section). Thermogravimetric analysis shows the presence of 23 H_2O, in accord with the findings of the elemental analysis. Incidentally, 23 hydrated water molecules are also present in the crystalline material, $Na_9P_2W_{15}Nb_3O_{62}\cdot 23H_2O\cdot 2CH_3CN$, as determined by single-crystal X-ray diffraction analysis.[11] Infrared measurements (Figure 1) confirm that the Dawson-type "$P_2M_{18}O_{62}^{n-}$" heteropolytungstate framework remains intact under the conditions of the synthesis.

Further solution characterization relied on multinuclear ^{31}P and ^{183}W NMR. A ^{31}P NMR spectrum of $Na_9P_2W_{15}Nb_3O_{62}$ in D_2O (Figure 2) shows primarily two resonances at δ −7.8 and −14.3 (± 0.2 ppm) with integrated intensities of 1:1 as expected for the two types of phosphorus present.[15] The downfield resonace (δ −7.8) is assigned to the phosphorus closest to the Nb_3O_6 site, whereas the upfield resonance at δ −14.3 is known to be due to the phosphorus closer to the W_3O_6 cap (Figure 4).[4g,h] The two-line ^{31}P NMR spectrum (Figure 2) requires the presence of a single species in solution and, therefore, precludes the existence of even minor impurities. It also excludes the presence of at least slowly interconverting ion pairs between Na^+ and $P_2W_{15}Nb_3O_{62}^{9-}$ in *aqueous solution*. In contrast, ion-pairing is commonly observed for non-aqueous solutions (CD_3CN, DMSO-d_6) of mixed salts such as $[(n\text{-}C_4H_9)_4N]_5Na_3[(1,5\text{-COD})Ir\cdot P_2W_{15}Nb_3O_{62}]$.[16]

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(15) In comparison, the following ^{31}P NMR shifts have been reported[4g] for related complexes: (a) $[(n\text{-}C_4H_9)_4N]_9P_2W_{15}Nb_3O_{62}$ (in CD_3CN), δ −7.3, −14.1; (b) $Li_{9-x}H_xP_2W_{15}Nb_3O_{62}$ (in D_2O), δ −8.0, −12.4.

(16) Pohl, M.; Lyon, D. K.; Nomiya, K.; Finke, R. G. Manuscript in preparation.

This in turn, ion-pairing, gives rise to multiple lines in the ^{31}P NMR.

The ^{183}W NMR spectrum of $Na_9P_2W_{15}Nb_3O_{62}$ in D_2O (Figure 3) shows primarily three peaks. The integrated intensities are 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, as expected for a Wells–Dawson heteropolyoxoanion (Figure 4).

The solid-state structure of $Na_9P_2W_{15}Nb_3O_{62}{\cdot}2CH_3CN{\cdot}23H_2O$, as determined by single-crystal X-ray diffraction crystallography, has previously been reported elsewhere.[11]

Summary

In summary, the water-soluble all sodium salt of the Dawson-type heteropolyoxoanion organometallics-support system, $Na_9P_2W_{15}Nb_3O_{62}{\cdot}23H_2O$, has been isolated, in 61% yield and on a 13-g scale, and has been unequivocally characterized, both in solution and (previously) in the solid state. Hence, the first step toward obtaining crystalline $P_2W_{15}Nb_3O_{62}^{9-}$-supported organometallic catalyst precursors has been accomplished. The title complex is also of interest as a possible new type of solid-base catalyst.[17]

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