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HIGH YIELD SYNTHESIS OF MIXED-METAL KEGGIN POLYOXOANIONS IN NON-AQUEOUS SOLVENTS: PREPARATION OF $(n\text{-}Bu_4N)_4[PMW_{11}O_{40}]$ (M = V, Nb, Ta)

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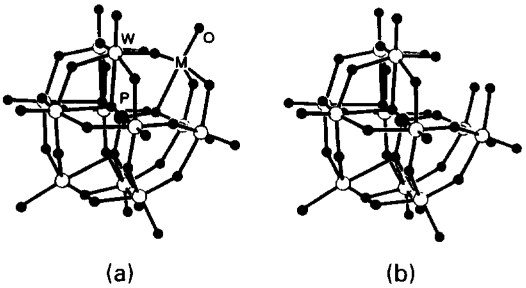
Abstract—The synthesis of $(n\text{-}Bu_4N)_4[PMW_{11}O_{40}]$ (M = V, Nb, Ta) in non-aqueous solvents is described using the lacunary compound $(n\text{-}Bu_4N)_4H_3[PW_{11}O_{39}]$ and commercially available $VOCl_3$, $NbCl_5$ and $TaCl_5$. The yield and purity of the product vary depending on the solvent and the presence of base. ^{183}W NMR spectroscopy of the title compounds reveal six resonances in the ratio 2 : 2 : 2 : 1 : 2 : 2 (M = Nb, Ta) consistent with their formulation as monosubstituted tungstophosphates with the Keggin structure. Their FAB mass spectra display protonated molecular ions in the positive ion mode and monoanionic fragments MO_x and $MW_nO_x (n \geqslant 1, x \geqslant n)$ (M = Nb, Ta) in the negative ion mode.

During the last two decades, remarkable progress in the synthesis of polyoxoanion derivatives has been made using non-aqueous solvents.[1] Many of these studies involve mixed-metal polyoxoanions in which a Group 5 metal is substituted for a Group 6 metal.[2–4] Each substitution adds a negative charge located primarily on the oxygens bound to the Group 5 metal.[1b] As a consequence, Group 5 substituted polyoxoanions exhibit enhanced basicity and reactivity at these oxygens and can be viewed as having a reactive $[M=O]^{3+}$ (M = V, Nb, Ta) fragment embedded into the inert tungstate framework.

In contrast, derivatives of monosubstituted Group 5 mixed-metal tungstophosphates with the Keggin structure[5] (Fig. 1a) have been little studied. In this paper, we describe a facile non-aqueous synthesis of the $n\text{-}Bu_4N^+$ salt of a mixed-metal Keggin ion in which a Group 5 metal centre fills the "gap" in a lacunary polyoxoanion composed of a Group 6 metal and oxygen atom framework (Fig. 1b). The $n\text{-}Bu_4N^+$ ion has proven to be a useful counterion to prepare soluble, well-defined polyoxoanion salts suitable for reactions in non-aqueous solutions. These syntheses employ the lacunary compound, $(n\text{-}Bu_4N)_4H_3[PW_{11}O_{39}]$ and commercially available $VOCl_3$, $NbCl_5$ or $TaCl_5$ to form $(n\text{-}Bu_4N)_4[PMW_{11}O_{40}]$ (M = V, Nb, Ta). The lacunary compound has been effective for preparing $(n\text{-}Bu_4N)_4[PW_{11}O_{39}(M''L)]$ (M'' = Ti, Zr, Tc, Re, Sn; L = $\eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5H_4R$, N, O, Cl).[6] Our method is an extension of this approach to the Group 5 metals. Existing methods for the preparation of $[PMW_{11}O_{40}]^{4-}$ ions include the preparation of $(n\text{-}Bu_4N)_4[PVW_{11}O_{40}]$ as a cation methathesis in water[7] and the $[PNbW_{11}O_{40}]^{4-}$ ion as the heteropolyacid[8] and its Me_4N^+ salt.[9] No synthesis of $[PTaW_{11}O_{40}]^{4-}$ has been reported.



(a) (b)

Fig. 1. Structural representation of (a) the monosubstituted mixed-metal polyoxoanion $[PMW_{11}O_{40}]^{4-}$ (M = V, Nb, Ta) and (b) the lacunary polyoxoanion $H_3[PW_{11}O_{39}]^{4-}$ (H atoms not shown). The oxygen radii are shown as smaller than the metal radii for clarity.

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EXPERIMENTAL

Materials and Methods

All reagents were used as received from commercial suppliers. Acetonitrile and pyridine were distilled from CaH_2 under dinitrogen prior to use. Elemental analyses (CHN) were performed by Robertson Microlit Labs (Madison, NJ). IR spectra were recorded on a Perkin–Elmer 1600 Series FTIR spectrometer. ^1H, ^{31}P and ^{51}V NMR spectra were acquired on a Varian VXR-300 spectrometer. ^{183}W NMR spectra were obtained on a JEOL GX-400 spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a JEOL JMS-DX 303 HF machine with Xe gas, 3 kV, resolution 1 : 1500 at 2300 m/z. Negative ion spectra were obtained with a dithiothreitol/dithioerythritol (5 : 1) matrix. Positive ion spectra were obtained using a 3-nitrobenzyl alcohol matrix.

Preparation of compounds

$(n\text{-}Bu_4N)_4H_3[PW_{11}O_{39}]$. This procedure is a slight modification of the synthesis by Ho and Klemperer[10] and affords a product which can be used without further purification.

$Na_2HPO_4 \cdot 7H_2O$ (1.48 g, 5.5 mmol) followed by 20.0 g (60.6 mmol) $Na_2WO_4 \cdot 2H_2O$ was dissolved with stirring in 40 cm^3 of water; 4 cm^3 of concentrated (12 M) HCl was then added in drops with stirring over 15 min. As the HCl was added, white flakes formed which were allowed to dissolve before adding more acid. The solution was stirred for 1 h at room temeprature during which a white precipitate formed. Approximately 4 cm^3 more of concentrated HCl was added with stirring until the pH reached 5.5 (measured with a combination pH electrode). The white precipitate dissolved by the end of the addition. For the next 30 min, the pH of the solution was monitored continuously and dilute HCl was added as necessary to maintain the pH between 5.0 and 5.5. A solution of 8.0 g (25 mmol) $(n\text{-}Bu_4N)Br$ in 60 cm^3 water was then added and precipitation of the product began at once. The precipitation was completed by adding approximately 6 cm^3 of 3M HCl dropwise with vigorous stirring until the pH of the solution remained between 1.1 and 1.2 for 5 min.

The product was filtered immediately on a coarse glass frit and washed with an abundant amount of water and then with diethyl ether. Any remaining moisture was removed by drying *in vacuo* for 24 h at 60°C. Yield: 20.0 g (99%). Found: C, 21.4; H, 3.8; N, 1.5. Calc. for $C_{64}H_{147}N_4PW_{11}O_{39}$: C, 21.1; H, 4.1; N, 1.5%. IR (KBr, cm^{-1}): 1107 (m), 1054 (m), 957 (vs), 886 (vs), 808 (vs), 754 (m), 596 (vw), 519 (w).

$(n\text{-}Bu_4N)_4[PVW_{11}O_{40}]$. $VOCl_3$ (0.240 g, 1.4 mmol) was added dropwise at room temperature to a stirred solution of 5.00 g (1.4 mmol) of $(n\text{-}Bu_4N)_4H_3[PW_{11}O_{39}]$ in 25 cm^3 pyridine under an inert atmosphere (exothermic). The reaction mixture was heated in a Schlenk tube under argon for 1 h at 80°C. Then it was cooled in water to room temperature and the brown solution was added with stirring to 300 cm^3 of diethyl ether to precipitate the product as a yellow powder. The product was washed with diethyl ether and dried *in vacuo*. Yield: 4.81 g (94%). The product was purified by recrystallization from hot acetonitrile. Found: C, 20.9; H, 3.9; N, 1.5. Calc. for $C_{64}H_{144}N_4PVW_{11}O_{40}$: C, 20.7; H, 3.9; N, 1.5%. IR (KBr, cm^{-1}): 1097 (s), 1070 (s), 995 (w), 962 (vs), 890 (vs), 809 (vs), 597 (vw), 520 (w), 505 (w).

$(n\text{-}Bu_4N)_4[PNbW_{11}O_{40}]$. $NbOCl_3 \cdot 2MeCN$ was prepared *in situ* by adding a solution of 0.225 g (1.4 mmol) hexamethyldisiloxane in 2 cm^3 acetonitrile to 0.375 g (1.4 mmol) $NbCl_5$ dissolved in 2.5 cm^3 acetonitrile in an inert atmosphere.[11] After stirring for 2 h at room temperature, this solution was added quickly to 5.00 g (1.4 mmol) of $(n\text{-}Bu_4N)_4H_3[PW_{11}O_{39}]$ in 40 cm^3 of acetonitrile. The reaction mixture was refluxed in air for 3 h in a round bottom flask fitted with a condenser and a drying tube filled with molecular sieves. The solution was cooled to room temeprature and was added to 300 cm^3 of diethyl ether to precipitate the product. Yield: 4.36 g (85%). Analytically pure product was obtained by recrystallization from acetonitrile. Found: C, 20.5; H, 3.9; N, 1.4. Calc. for $C_{64}H_{144}N_4PNbW_{11}O_{40}$: C, 20.5; H, 3.9; N, 1.5%. IR (KBr, cm^{-1}): 1083 (s), 1070 (s), 965 (vs), 941 (w), 889 (vs), 808 (vs), 595 (vw), 518 (w), 505 (w).

$(n\text{-}Bu_4N)_4[PTaW_{11}O_{40}]$. $TaCl_5$ (0.495 g, 1.4 mmol) was dissolved with stirring in 25 cm^3 of pyridine under an inert atmosphere (exothermic). The solution was added to a stirring suspension of 4 g (38 mmol) of anhydrous Na_2CO_3 in 25 cm^3 pyridine containing 5.00 g (1.4 mmol) of $(n\text{-}Bu_4N)_4H_3[PW_{11}O_{39}]$ and 0.025 g (1.4 mmol) of water. The reaction mixture was stirred for 24 h at room temperature. All subsequent manipulations were carried out in air. Any remaining solid was separated by centrifugation and the solution, containing the product, was treated as in the case of $(n\text{-}Bu_4N)_4[PVW_{11}O_{40}]$. Yield: 4.73 g (90%). Found: C, 20.1; H, 3.8; N, 1.4. Calc. for $C_{64}H_{144}N_4PTaW_{11}O_{40}$: C, 20.0; H, 3.8; N, 1.5%. IR (KBr, cm^{-1}): 1072 (vs), 966 (vs), 941 (w), 892 (vs), 808 (vs), 595 (vw), 518 (w), 508 (w).

RESULTS AND DISCUSSION

Synthesis of $(n\text{-Bu}_4\text{N})_4[\text{PMW}_{11}\text{O}_{40}]$ (M = V, Nb, Ta)

The mixed-metal polyoxoanions $(n\text{-Bu}_4\text{N})_4[\text{PMW}_{11}\text{O}_{40}]$ (M = V, Nb, Ta) were prepared by reacting MOCl_3 (M = V, Nb) or MCl_5 (M = Nb, Ta) and H_2O (M = Nb, Ta) with the lacunary compound $(n\text{-Bu}_4\text{N})_4\text{H}_3[\text{PW}_{11}\text{O}_{39}]$ as shown in reactions (1) and (2). The crude products contained small amounts (typically <5%) of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ as detected by ^{31}P NMR spectroscopy. This side product could be removed easily by recrystallization in acetonitrile because of its different charge.

$$(n\text{-Bu}_4\text{N})_4\text{H}_3[\text{PW}_{11}\text{O}_{39}]+\text{MOCl}_3 \rightarrow \underset{\text{M = V,Nb}}{(n\text{-Bu}_4\text{N})_4[\text{PMW}_{11}\text{O}_{40}]}+3\text{HCl} \quad (1)$$

$$(n\text{-Bu}_4\text{N})_4\text{H}_3[\text{PW}_{11}\text{O}_{39}]+\text{MCl}_5+\text{H}_2\text{O} \rightarrow \underset{\text{M = Nb,Ta}}{(n\text{-Bu}_4\text{N})_4[\text{PMW}_{11}\text{O}_{40}]}+5\,\text{HCl} \quad (2)$$

The formation of $(n\text{-Bu}_4\text{N})_3[\text{PW}_{12}\text{O}_{40}]$ is most likely due to a reaction between $(n\text{-Bu}_4\text{N})_4\text{H}_3[\text{PW}_{11}\text{O}_{39}]$ and HCl generated during the synthesis. When pyridine was used as a solvent instead of acetonitrile, a significant improvement in the yield and purity of $(n\text{-Bu}_4\text{N})_4[\text{PMW}_{11}\text{O}_{40}]$ (M = V, Ta) was obtained. The formation of $(n\text{-Bu}_4\text{N})_3[\text{PW}_{12}\text{O}_{40}]$ during the preparation of $(n\text{-Bu}_4\text{N})_4[\text{PNbW}_{12}\text{O}_{40}]$ in acetonitrile was small enough to render the synthesis in that solvent practical.

The formation of $(n\text{-Bu}_4\text{N})_3[\text{PW}_{12}\text{O}_{40}]$ was also reduced by adding a non-aqueous base. The addition of triethylamine or 1,8-bis(dimethylamino)naphthalene (Proton Sponge) in reaction (2) allowed quantitative conversion of $\text{H}_3[\text{PW}_{11}\text{O}_{39}]^{4-}$ to $[\text{PMW}_{11}\text{O}_{40}]^{4-}$ (M = Nb, Ta) by ^{31}P NMR spectroscopy. This was not a convenient method of preparation, however, because the product was contaminated with the corresponding ammonium cations as observed by ^{1}H NMR spectroscopy. The yield of $(n\text{-Bu}_4\text{N})_4[\text{PTaW}_{11}\text{O}_{40}]$ was particularly susceptible to HCl, so the addition of anhydrous Na_2CO_3 to the reaction mixture made it possible to obtain both a high yield and purity. In contrast, the yield of $(n\text{-Bu}_4\text{N})_4[\text{PNbW}_{11}\text{O}_{40}]$ according to reaction (2) was poor in the presence of Na_2CO_3.

Characterization of $(n\text{-Bu}_4\text{N})_4[\text{PMW}_{11}\text{O}_{40}]$ (M = V, Nb, Ta)

The solution characterization of $(n\text{-Bu}_4\text{N})_4[\text{PMW}_{11}\text{O}_{40}]$ was aided by the presence of several NMR active nuclei. The ^{1}H NMR spectra of all the compounds are identical and display resonances due solely to the n-tetrabutylammonium cation. ^{31}P and ^{183}W NMR spectroscopic data of $(n\text{-Bu}_4\text{N})_4[\text{PMW}_{11}\text{O}_{40}]$ are given in Table 1. All the ^{31}P NMR resonances are sharp singlets and range from 1 to 2 ppm upfield from $(n\text{-Bu}_4\text{N})_4\text{H}_3[\text{PW}_{11}\text{O}_{39}]$ (−11.7 ppm). This interval agrees with the finding that small upfield shifts are observed when a metal is added to the lacunary compound.[9] The ^{51}V NMR spectrum of 0.1 M $(n\text{-Bu}_4\text{N})_4[\text{PVW}_{11}\text{O}_{40}]$ in DMF displays a single resonance at 547 ppm upfield from VOCl_3. This chemical shift is in good agreement with the published value of 545 ppm.[12]

More structural information is provided by the ^{183}W NMR spectra summarized in Table 1. The C_s symmetry of the $[\text{PMW}_{11}\text{O}_{40}]^{4-}$ ion implies that a total of six resonances should be observed in the ^{183}W NMR spectra corresponding to five magnetically inequivalent pairs of tungsten atoms and a unique tungsten atom.[13] The spectra of $(n\text{-Bu}_4\text{N})_4[\text{PMW}_{11}\text{O}_{40}]$ (M = Nb, Ta) are consistent with the symmetry requirement. The ^{183}W NMR spectrum of $(n\text{-Bu}_4\text{N})_4[\text{PVW}_{11}\text{O}_{40}]$ spectrum is clearly different. One of the resonances due to a pair of tungsten atoms is absent and another one at −60 ppm is broadened due to an interaction with ^{51}V. This observation concurs with the reported spectrum of the $[\text{PVW}_{11}\text{O}_{40}]^{4-}$ ion.[14]

Finke and co-workers have demonstrated that fast atom bombardment mass spectroscopy (FAB-MS) is a powerful technique for the study of polyoxoanions.[15] Since the CHN elemental analyses of $(n\text{-Bu}_4\text{N})_4[\text{PMW}_{11}\text{O}_{40}]$ (M = V, Nb, Ta) do not differ significantly from each other or the lacunary starting material, this technique was chosen to fur-

Table 1. ^{31}P and ^{183}W NMR spectra of $(n\text{-Bu}_4\text{N})_4[\text{PMW}_{11}\text{O}_{40}]$

	Chemical shift, δ (ppm)		
	M = V	M = Nb	M = Ta
^{31}P NMR[a]	−13.7	−12.7	−13.4
^{183}W NMR[b]	−60.0(2W) −86.0(2W) −87.7(2W) −91.7(1W) −96.8(2W)	−62.1(2W) −82.9(2W) −87.8(2W) −92.7(1W) −93.8(2W) −101.3(2W)	−62.5(2W) −81.6(2W) −88.0(2W) −93.2(1W) −95.7(2W) −100.6(2W)

[a] 0.1 M solution in DMF (upfield from external reference: 85% H_3PO_4).

[b] 0.1 M solution of d_6-DMSO (upfield from external reference: satd. Na_2WO_4 in D_2O at 20°C).

ther characterize the products. In the negative ion mode, extensive fragmentation takes place while in the positive ion mode the protonated molecular ions can be observed.[16] The negative FAB mass spectra of $(n\text{-Bu}_4\text{N})_4[\text{PMW}_{11}\text{O}_{40}]$ (M = V, Nb, Ta) consist of progressions of peak envelopes separated by 16 m/z units corresponding to the loss of oxygen atoms.

For a given envelope, the peak distribution is determined largely by the number of tungsten atoms in the corresponding fragment since all other elements involved either consist of a single nuclide or have one isotope of at least 99% natural abundance. In all cases, envelopes corresponding to fragments of the general formula W_nO_x ($n \geqslant 1$, $x \geqslant n$) were observed. The spectra of $(n\text{-Bu}_4\text{N})_4[\text{PMW}_{11}\text{O}_{40}]$ (M = Nb, Ta) also exhibit series of MO_x peaks with intensities an order of magnitude lower than the WO_x series, consistent with the 1 : 11 M to W ratio in $(n\text{-Bu}_4\text{N})_4[\text{PMW}_{11}\text{O}_{40}]$.

Further evidence for the incorporation of the Group 5 metal into the poloxyoanion is supplied by the appearance of the NbW_nO_x and TaW_nO_x series. The former can be seen separately from the W_nO_x series while the latter are detected by the additional peak in the W_nO_x envelopes due to ^{181}Ta. No VW_nO_x envelopes could be identified because of overlap with those of the W_nO_x series. Since the atomic mass of ^{31}P is close to the mass of two ^{16}O atoms, it could not be determined whether these fragments contained phosphorus at the level of resolution of these FAB spectra.

The positive ion FAB-MS of $(n\text{-Bu}_4\text{N})_4[\text{PMW}_{11}\text{O}_{40}]$ (M = V, Nb, Ta) shows the molecular ion envelopes for $(n\text{-Bu}_4\text{N})_4[\text{PMW}_{11}\text{O}_{40}]\cdot\text{H}^+$ as well as envelopes corresponding to $(n\text{-Bu}_4\text{N})_5[\text{PMW}_{11}\text{O}_{40}]\cdot\text{H}^+$ and $(n\text{-Bu}_4\text{N})_6[\text{PMW}_{11}\text{O}_{40}]\cdot\text{H}^+$, formed presumably by one- and two-electron reduction of the anions. Due to the relatively large number of tungsten atoms present, all these envelopes have a nearly Gaussian peak distribution with a width at half-height of approximately 8 m/z units.

CONCLUSIONS

A direct method of obtaining mixed-metal polyoxoanions soluble in polar organic solvents can be achieved by combination of the lacunary compound $(n\text{-Bu}_4\text{N})_4\text{H}_3[\text{PMW}_{11}\text{O}_{39}]$ and convenient Group 5 starting materials. The major side product of these reactions, $(n\text{-Bu}_4\text{N})_3[\text{PMW}_{12}\text{O}_{40}]$, can be reduced significantly or eliminated by varying the solvent or the addition of base. The products have ^{51}V, ^{31}P and ^{183}W NMR spectroscopic parameters that are consistent with their formulation as $(n\text{-Bu}_4\text{N})_4[\text{PMW}_{11}\text{O}_{40}]$ (M = V, Nb, Ta). Positive and negative ion FAB mass spectroscopy has proven to be a valuable method for characterizing these species.

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