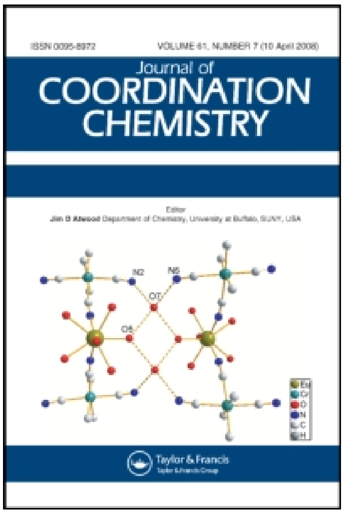

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Synthesis and spectroscopic characterization of organophosphoryl polyoxotungstates α-[PhP(Y)]$_2$X*ⁿ*$^+$W$_{11}$

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Synthesis and spectroscopic characterization of organophosphoryl polyoxotungstates α-$[PhP(Y)]_2X^{n+}W_{11}O_{39}^{(8-n)-}$

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Organophosphoryl polyoxotungstate derivatives α-$[PhP(Y)]_2X^{n+}W_{11}O_{39}^{(8-n)-}$ ($X^{n+} = Ge^{4+}, B^{3+}$; $Y = O, S$) have been obtained by the reaction of the monovacant α-$[X^{n+}W_{11}O_{39}]^{(12-n)-}$ ($X^{n+} = Ge^{4+}, B^{3+}$) anions with $PhP(O)Cl_2$ or $PhP(S)Cl_2$ in acetonitrile. These new organic–inorganic hybrid anions have been characterized by elemental analysis, IR, ^{31}P and ^{183}W NMR spectroscopy. According to the elemental analysis and spectroscopic data, the hybrid anions consist of an α-$[XW_{11}O_{39}]$ framework on which are grafted two equivalent PhP(O) or PhP(S) groups through P–O–W bridges. The six-line ^{183}W NMR spectrum indicates that the hybrid anions possess C_s symmetry in acetonitrile.

Keywords: Polyoxometalate; Organophosphorus; Syntheses; NMR (^{31}P; ^{183}W)

1. Introduction

Interest and activity in derivatized polyoxometalates (POMs), especially those including organic and organometallic components, is largely stimulated by their potential applications in catalysis, medicine and material science [1–3]. It has been recognized for a long time that the introduction of organic groups into the POM framework could greatly increase the number of compounds available for screening, and provides a potential modulation of essential features, such as stability, bioavailability, and recognition [4].

Several research groups have used a variety of approaches to incorporate organic or organometallic moieties in polyoxoanion frameworks, and many organic-derivatized POMs have been synthesized and characterized [5]. But, to the best of the authors' knowledge, organophosphorus-substituted heteropolyanions have been rarely reported.

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Hill and coworkers were the first to study the interaction of organophosphorus groups with polyoxoanions, reporting the formation of hybrid derivatives $[PhP(O)]_2X^{n+}W_{11}O_{39}^{(8-n)-}$ ($X^{n+} = P^{5+}, Si^{4+}$) [6]. As an extension of this work, the authors recently investigated the reactivity of organophosphonic acids $RPO(OH)_2$ or organophosphonoyl dichloride $RP(O)Cl_2$ with the lacunar polyoxotungstates [7–9]. In all these hybrid anions, two RPO groups are grafted on the surface of the POM framework through two P–O–W bridges, resulting in partial saturation of the polyoxotungstates. Studies on organophosphoryl derivatives of α-$[XW_{11}O_{39}]$ (X = Ge, B) have not yet been reported. In this article, the syntheses and spectroscopic properties of organic–inorganic hybrid anions α-$[PhP(Y)]_2X^{n+}W_{11}O_{39}^{(8-n)-}$ ($X^{n+} = Ge^{4+}, B^{3+}$; Y = O, S) are reported. The structure characterization of these new species was performed by means of IR, ^{31}P and ^{183}W NMR spectroscopy.

2. Experimental

2.1. *Syntheses*

2.1.1. Preparation of α-$[Bu_4N]_4H[PhP(O)]_2BW_{11}O_{39}$ (1). α-$K_7NaHBW_{11}O_{39} \cdot 13H_2O$ (2.54 g, 0.8 mmol) and Bu_4NBr (1.29 g, 4 mmol) were suspended in acetonitrile (25 mL), to which an acetonitrile solution of $PhP(O)Cl_2$ (0.24 mL, 1.6 mmol in 15 mL of acetonitrile) was added dropwise under vigorous stirring. The solution turned pale yellow, and the mixture was stirred for 24 h at room temperature. After filtration of a white solid, the resulting yellow solution was concentrated on a rotary evaporator to ca 10 mL. To the concentrated solution 100 mL of anhydrous Et_2O was added with stirring to produce a yellow oily deposit. The turbid supernatant was decanted from the oily deposit, which was redissolved in 5 mL of acetonitrile. The solution was then diluted with 100 mL of anhydrous Et_2O, and a white powder was obtained. The solid was filtered off, washed with anhydrous Et_2O, and air-dried.

Yield 45.3%. Anal. Calcd for $C_{76}H_{155}BN_4O_{41}P_2W_{11}$ (%): C, 23.5; H, 4.01; N, 1.45; B, 0.28; P, 1.60; W, 51.9. Found: C, 23.3; H, 3.85; N, 1.39; B, 0.25; P, 1.67; W, 51.6. Selected IR bands (2000–400 cm^{-1} region): 1144, 903, 967, 829, 768. ^{31}P NMR (CD_3CN): δ 20.5.

2.1.2. Preparation of α-$[Bu_4N]_3H[PhP(O)]_2GeW_{11}O_{39}$ (2). This compound was similarly synthesized as a white powder from α-$K_6Na_2GeW_{11}O_{39} \cdot 13H_2O$ (2.58 g, 0.8 mmol), Bu_4NBr (1.29 g, 4 mmol) and $PhP(O)Cl_2$ (0.24 mL, 1.6 mmol).

Yield 50.7%. Anal. Calcd for $C_{60}H_{119}GeN_3O_{41}P_2W_{11}$ (%): C, 19.5; H, 3.22; N, 1.13; Ge, 1.98; P, 1.68; W, 54.8. Found: C, 19.4; H, 3.15; N, 1.09; Ge, 1.87; P, 1.73; W, 55.1. Selected IR bands (2000–400 cm^{-1} region): 1137, 892, 972, 879, 778. ^{31}P NMR (CD_3CN): δ 17.6.

2.1.3. Preparation of α-$[Bu_4N]_4H[PhP(S)]_2BW_{11}O_{39}$ (3). α-$K_7NaHBW_{11}O_{39} \cdot 13H_2O$ (1.59 g, 0.5 mmol) and Bu_4NBr (0.81 g, 2.5 mmol) were suspended in acetonitrile (25 mL), to which an acetonitrile solution of $PhP(S)Cl_2$ (0.15 mL, 1.0 mmol in 10 mL of acetonitrile) was added dropwise under vigorous stirring, and the mixture was stirred for 48 h at room temperature. After filtration of a white solid, the resulting red solution was concentrated by rotary evaporation to ca 10 mL. To the solution

150 mL of absolute ethanol was added with stirring to produce a red brown precipitate. The precipitate was isolated by filtration, and the solid isolated was reprecipitated again from 5 mL of acetonitrile solution by adding 100 mL of absolute ethanol to give a red brown powder.

Yield 67.1%. Anal. Calcd for $C_{76}H_{155}BN_4O_{39}P_2S_2W_{11}$ (%): C, 22.8; H, 3.84; N, 1.40; B, 1.75; P, 1.55; W, 50.6. Found: C, 22.4; H, 3.61; N, 1.35; B, 1.62; P, 1.63; W, 51.0. Selected IR bands (2000–400 cm^{-1} region): 1151, 898, 963, 829, 789. ^{31}P NMR (CD_3CN): δ 71.6. ^{183}W NMR (CD_3CN): δ −92.3(2), −111.4(2), −116.1(1), −123.2(2), −191.5(2) and −197.2(2).

2.1.4. Preparation of α-$[Bu_4N]_3H[PhP(S)]_2GeW_{11}O_{39}$ (4). α-$K_6Na_2GeW_{11}O_{39} \cdot 13H_2O$ (2.58 g, 0.8 mmol) and Bu_4NBr (1.29 g, 4 mmol) were suspended in acetonitrile (25 mL), an acetonitrile solution of $PhP(S)Cl_2$ (0.24 mL, 1.6 mmol in 10 mL of acetonitrile) was added dropwise under vigorous stirring, and the mixture was stirred for 48 h at room temperature. After filtration of a white solid, the yellow compound was obtained by evaporation of the resulting solution in air. The crude product was recrystallized from acetonitrile.

Yield 37%. Anal. Calcd for $C_{60}H_{119}GeN_3O_{39}P_2S_2W_{11}$ (%): C, 19.3; H, 3.19; N, 1.13; Ge, 1.96; P, 1.66; W, 54.3. Found: C, 19.1; H, 3.04; N, 1.08; Ge, 1.87; P, 1.74; W, 54.7. Selected IR bands (2000–400 cm^{-1} region): 1149, 899, 964, 836, 787. ^{31}P NMR (CD_3CN): δ 68.6.

2.2. *Materials*

All reagents were of analytical or guaranteed purity. CH_3CN was distilled over P_2O_5 and used immediately. α-$K_6Na_2GeW_{11}O_{39} \cdot 13H_2O$ and α-$K_7NaHBW_{11}O_{39} \cdot 13H_2O$ were prepared from literature methods [10]. $PhP(O)Cl_2$ and $PhP(S)Cl_2$ were prepared according to a published method [11]. Their purity was checked by IR or ^{31}P NMR spectroscopy.

2.3. *Physical measurements*

C, H, and N were determined using a PE-2400 elemental analyzer, Na, K, B, Ge, P and W were determined using an inductively coupled plasma (ICP) atomic absorption spectrometer. The IR spectra were recorded on an Alpha Centauri FTIR spectrometer (2000–400 cm^{-1} range) with KBr pellets. The ^{31}P NMR spectra were recorded with a JNM-FX-100 NMR spectrometer, and chemical shifts were given with respect to external 85% H_3PO_4 for ^{31}P in CD_3CN. The ^{183}W NMR spectrum was recorded at 16.64 MHz on a Unity-400 spectrometer by using a 10 mm diameter NMR tube at 20°C, the chemical shifts were referenced to 2 M Na_2WO_4 in D_2O for ^{183}W.

3. Results and discussion

3.1. *IR spectra*

The infrared spectra of all the compounds are very similar. The highest wavenumbers (1137–1151 cm^{-1}) are assigned to the stretching vibrations of the P–C bond of organophosphorus unit, the peaks at the low wavenumber region ($\nu < 1000\ cm^{-1}$) are

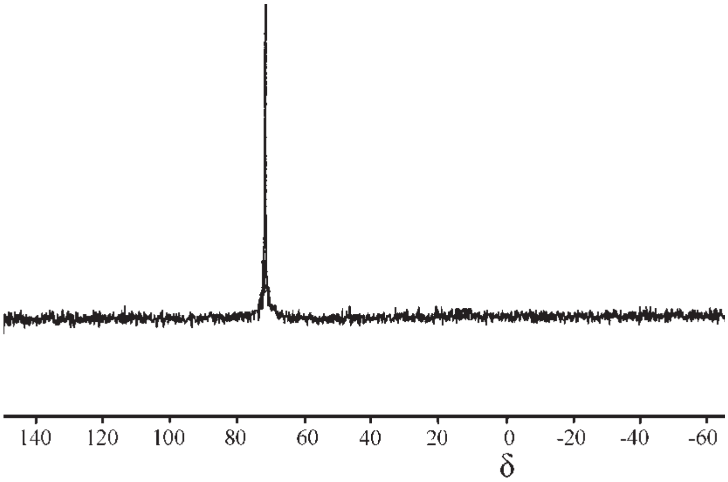

Figure 1. ^{31}P NMR spectrum of α-$[Bu_4N]_4H[PhP(S)]_2BW_{11}O_{39}$.

characteristic of the W–O stretching and bending vibration in the polyoxotungstate framework. The IR spectra of all the compounds exhibit the four characteristic W–O_d, W–O_b–W, W–O_c–W and X–O_a (X = B, Ge) asymmetric stretching vibrational bands for heteropolyanions with the Keggin structure, suggesting that the polyoxometallic moiety of the title compounds still retains the basic framework of the Keggin structure.

3.2. ^{31}*P NMR spectra*

The attachment of organophosphoryl groups onto the polyoxotungstate surface is also demonstrated by ^{31}P NMR spectra (see figure 1).

The ^{31}P NMR spectra of the title compounds exhibit only a single line, indicating that the two PhP(Y) groups on the lacunar anions are equivalent. For example, tetrabutylammonium salt of α-$[PhP(S)]_2BW_{11}O_{39}^{5-}$ in CD_3CN displays a single, sharp resonance at δ 71.6, in lower field by comparison with that of $PhP(S)Cl_2$ (δ 75.6). A heteropolyanion with a Keggin structure becomes the C_s lacunary polyanion $[X^{n+}W_{11}O_{39}]^{(12-n)-}$ after losing one heavy atom and its terminal oxygen, containing three W_3O_{13} triads and one W_2O_{10} diad. These anions have a hole surrounded by five oxygen atoms, one O_a, two O_b and two O_c (see figure 2a). When two double bonded phosphoryl groups each bridges two of the five oxygen atoms that define the hole in the lacunar polyanion, the groups can bridge the oxygens such that they are either inequivalent or equivalent. The single resonance in the ^{31}P NMR spectra indicates that the mode of attachment of the organic groups to the lacunar anion is equivalent, i.e. each organic group is connected to two oxygen atoms belonging to a triad and a diad, respectively (see figure 2b).

3.3. ^{183}*W NMR spectrum*

The ^{183}W NMR spectrum (see figure 3) of compound **3** consists of six peaks with relative intensity ratios of 2 : 2 : 1 : 2 : 2 : 2, and chemical shifts are −92.3, −111.4,

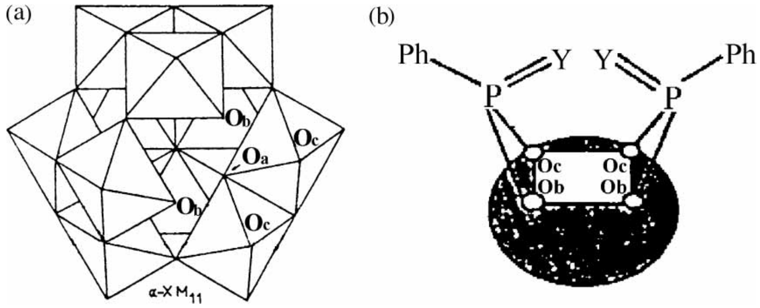

Figure 2. Schematic representation of α-[RP(Y)]$_2$X^{n+}W$_{11}$O$_{39}$$^{(8-n)-}$.

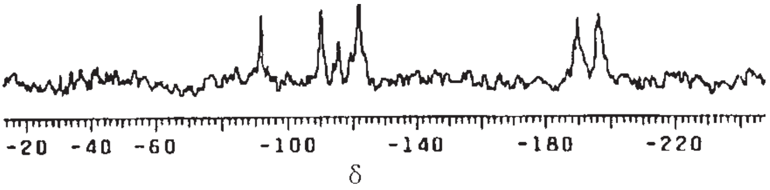

Figure 3. ^{183}W NMR spectrum of α-[Bu$_4$N]$_4$H[PhP(S)]$_2$BW$_{11}$O$_{39}$.

−116.1, −123.2, −191.5 and −197.2, respectively, indicating that the title compounds possess C_s symmetry in acetonitrile. This feature was observed for PhPO derivatives of monovacant Keggin-type tungstophosphate and tungstosilicate [6].

Synthesis of organic–inorganic hybrid anions α-[PhP(Y)]$_2$X^{n+}W$_{11}$O$_{39}$$^{(8-n)-}$ ($X^{n+} = Ge^{4+}, B^{3+}$; $Y = O, S$) has been performed by reacting PhP(O)Cl$_2$ or PhP(S)Cl$_2$ with lacunary heteropolyanions α-[X^{n+}W$_{11}$O$_{39}$]$^{(12-n)-}$ ($X = Ge, B$) in acetonitrile, using Bu$_4$NBr acting as a phase-transfer reagent. Elemental analysis results are consistent with the formulation of the title compounds. The reaction is

$$\alpha\text{-}[\mathrm{X}^{n+}\mathrm{W}_{11}\mathrm{O}_{39}]^{(12-n)-} + \mathrm{PhP(Y)Cl}_2 \xrightarrow[\mathrm{Bu_4NBr}]{\mathrm{MeCN}} \alpha\text{-}[\mathrm{PhP(Y)}]_2\mathrm{X}^{n+}\mathrm{W}_{11}\mathrm{O}_{39}^{(8-n)-}$$

Despite all efforts to grow suitable crystals of the PhP(Y) ($Y = O, S$) derivatives of α-[X^{n+}W$_{11}$O$_{39}$]$^{(12-n)-}$ ($X^{n+} = Ge^{4+}, B^{3+}$), a good sample for X-ray diffraction study was not successfully obtained. Thus the title compounds have to be characterized in solid state by IR spectroscopy and in the CD$_3$CN solution by ^{31}P and ^{183}W NMR spectroscopy. The collective application of spectroscopic data shows that the hybrid anions consist of an α-[XW$_{11}$O$_{39}$] framework on which are grafted two equivalent organophosphoryl groups through P–O–W bridges; each organophosphoryl group is connected to two oxygen atoms belonging to a triad and a diad, respectively. These new species still retain the basic framework of the Keggin structure.

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