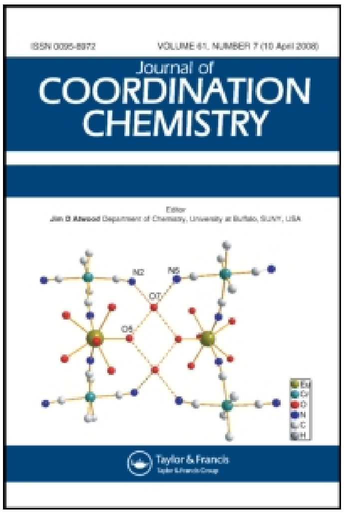

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Synthesis, spectroscopic properties and crystal structure of organophosphoryl polyoxotungstate α-$[Bu_4N]_3H[PhCH_2P(O)]_2SiW_{11}O_{39}$

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Synthesis, spectroscopic properties and crystal structure of organophosphoryl polyoxotungstate α-$[Bu_4N]_3H[PhCH_2P(O)]_2SiW_{11}O_{39}$

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Reaction of the monovacant heteropolyanions α-$[SiW_{11}O_{39}]^{8-}$ with $PhCH_2PO(OH)_2$ leads to the formation of the organophosphoryl derivative α-$[Bu_4N]_3H[PhCH_2P(O)]_2SiW_{11}O_{39}$ (**1**). Single-crystal X-ray diffraction analysis shows that the crystal is monoclinic with space group $P2_1/n$ and the unit cell parameters: $a = 14.386$ (3) Å, $b = 27.015$ (5) Å, $c = 25.480$ (5) Å, $\alpha = 90°$, $\beta = 91.44$ (3)°, $\gamma = 90°$, $V = 9899$ (3) Å^3. $Z = 4$, $D_c = 2.467\,g\,cm^{-1}$, λ (Mo-Kα) = 0.071073 nm, $R_1 = 0.0638$, $wR_2 = 0.1364$. The hybrid anion consists of an α-$[SiW_{11}O_{39}]^{8-}$ framework on which two equivalent organophosphoryl groups are grafted through P–O–W bridges; each of the two $PhCH_2P(O)$ groups are connected to two terminal oxygen atoms belonging to a triad and a diad, respectively.

Keywords: Polyoxometalate; Organophosphorus; Crystal structure; Synthesis

1. Introduction

Derivatized polyoxometalates, especially those including organic and organometallic components, have received increasing attention owing to their potential applications in catalysis, medicine and materials science [1–3]. The great variety of structures and the possibilities of modifying these for specific purposes ensure continued emphasis on synthesis, characterization, and reactivity studies. It has long been recognized that the ability to functionalize polyoxometalate anions would extend their versatility and lead to new and more selective applications. In the case of organic and organometallic derivatives, the properties of the polyoxometalate framework may be finely tuned

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by grafting appropriate organic and organometallic groups onto the polyoxometalate surface [4, 5].

During the past few years, several research groups have directed their efforts toward the synthesis of organic and organometallic derivatives of polyoxometalates [6]. But, to the best of our knowledge, the organophosphorus-substituted lacunary Keggin-type POMs have been rarely reported. Hill and co-workers were the first to study the formation of hybrid derivatives $[PhP(O)]_2X^{n+}W_{11}O_{39}{}^{(8-n)-}$ ($X^{n+} = P^{5+}, Si^{4+}$), and reported the first single crystal X-ray structure of phenylphosphonyl heteropolyundecatungstate [7]. In the course of our investigations of polyoxometalates derivatized with organic groups, we have examined the reaction of organophosphonic acids $RPO(OH)_2$ with a variety of lacunary polyoxotungstates; the characterization of these species is based on IR, ^{31}P and ^{183}W NMR spectroscopy [8–11]. In all these hybrid anions, two RPO groups are grafted on the surface of polyoxometalate framework through P–O–W bridges, resulting in the partial saturation of lacunary polyoxoanions. In order to further understand the structure of organophosphoryl polyoxometalates, we recently devoted effort toward preparation of single-crystals of organophosphorus-substituted heteropolyanions suitable for X-ray diffraction study. In this article, we report the syntheses, spectroscopic properties and single-crystal structure analysis of organic–inorganic hybrid α-$[Bu_4N]_3H[PhCH_2P(O)]_2SiW_{11}O_{39}$ **(1)**.

2. Experimental

2.1. *Materials*

All reagents were of analytical or guaranteed purity, CH_3CN was distilled over P_2O_5, and used immediately. $PhCH_2PO(OH)_2$ was prepared according to the published method [12]. α-$[Bu_4N]_4KH_3SiW_{11}O_{39}$ was prepared using procedures described in the literatures [7]. Their purity was checked by IR or ^{31}P NMR spectroscopy.

2.2. *Synthesis of α-$[Bu_4N]_3H[PhCH_2P(O)]_2SiW_{11}O_{39}$ (1)*

Single crystals of compound **1** have been obtained by reacting organophosphonic acid $PhCH_2PO(OH)_2$ with α-$[Bu_4N]_4KH_3SiW_{11}O_{39}$ in acetonitrile. In a typical synthesis, α-$[Bu_4N]_4KH_3SiW_{11}O_{39}$ (2.95 g, 0.8 mmol) was dissolved in acetonitrile (35 mL) and two equivalents (0.28 g, 1.6 mmol) of organophosphonic acid $PhCH_2PO(OH)_2$ was added under vigorous stirring, 12 M hydrochloric acid solution (0.27 mL, 3.2 mmol) was then added dropwise and the mixture was refluxed overnight. The yellow crystals were obtained by evaporation of the resulting solution in air and the crude product was recrystallized from hot acetonitrile. The filtrate was kept for 5 days at ambient conditions, the yellow block crystals of compound **1** suitable for X-ray diffraction study were obtained.

Yield: 55.8%. Anal. Calcd for $C_{62}H_{121}N_3O_{41}P_2SiW_{11}$ (%): C, 20.23; H, 3.34; N, 1.14; Si, 0.76; P, 1.68; W, 56.03. Found: C, 19.86; H, 3.31; N, 1.08; Si, 0.74; P, 1.72; W, 56.31. Selected IR bands (2000–400 cm^{-1} region): 916, 977, 891, 813, 732. ^{31}P NMR (CD_3CN): δ 25.9.

2.3. *Physical measurements*

C, H, N were determined by using a PE–2400 elemental analyzer. P, Si and W were determined by using an inductively coupled plasma (ICP) atomic absorption spectrometer (Plasma–Spec–II, USA). The IR spectrum was recorded on an Alpha Centauri FTIR spectrometer (2000–400 cm^{-1} range) with KBr pellets. The ^{31}P NMR spectrum was recorded at 16.64 MHz on a Unity-400 spectrometer, and chemical shifts are given with respect to external 85% H_3PO_4 for ^{31}P in CD_3CN.

2.4. *Crystal structure determination*

Crystal data: $C_{62}H_{121}N_3O_{41}P_2SiW_{11}$, $M = 3677.00$, monoclinic, space group $P2_1/n$, $a = 14.386$ (3) Å, $b = 27.015$ (5) Å, $c = 25.480$ (5) Å, $\alpha = 90°$, $\beta = 91.44$ (3)°, $\gamma = 90°$, $V = 9899$ (3) Å^3, $Z = 4$, $D_c = 2.467\ \mathrm{Mg\,m^{-3}}$, $F(0\,0\,0) = 6800$, λ (Mo-Kα) = 0.71073 Å, $T = 293$ K. A well-grown crystal of dimensions $0.52 \times 0.32 \times 0.24\ \mathrm{mm}^3$ was fixed inside a glass capillary. The intensity data were collected on a Siemens P4 four-circle diffractometer with the ω–2θ scan mode, in the range of $1.51° < \theta < 22.99°$. A total of 16,900 (13,713 independent, $R_{\mathrm{int}} = 0.0298$) reflections were measured. Structure solution and refinement based on 13,713 independent reflections with $I \geq 2\sigma(I)$ and 1064 parameters gave R_1 (wR_2) = 0.0638 (0.1364). The structure was solved by direct methods and refined by the full-matrix least-squares method on F^2. All calculations were performed by using the SHELXTL-97 program. A summary of the X-ray crystal data for compound **1** is shown in table 1. Selected bond lengths and bond angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structure*

The polyoxoanion of compound **1** exhibits a classical Keggin-type structure. In the polyoxoanion, the central Si atom is surrounded by a tetrahedron in which oxygen (O) vertices are linked to three W_3O_{13} triads and one W_2O_{10} diad, respectively. Each W_3O_{13} or W_2O_{10} consists of three or two WO_6 octahedra linked by sharing edges (O_c), and three W_3O_{13} triads and one W_2O_{10} diad moieties are linked together by sharing corners (O_b). There is a terminal oxygen atom (O_d) in every WO_6 octahedron. The bond lengths are as follows: the Si–O_a bond lengths range from 1.584 (9) to 1.677 (12) Å (av. 1.635 Å), the W=O_d bond lengths range from 1.641 (9) to 1.722 (10) Å (av. 1.673 Å), and the W–$O_{c,b}$ bond lengths range from 1.838 (10) to 1.998 (11) Å (av. 1.909 Å). The O–Si–O bond angles are in the 104.9 (5)°–112.6 (5)°, indicating that the SiO_4 tetrahedron is distorted. In compound **1** the P–O (organophosphorus unit) bond lengths are in the normal range of 1.512 (11)–1.566 (11) Å, and the P–O distances are as follows: P(1)–O(12) 1.514 (12), P(1)–O(13) 1.524 (11), P(1)–O(2) 1.566 (11), P(2)–O(14) 1.512 (11), P(2)–O(6) 1.527 (10) and P(2)–O(15) 1.532 (11) Å. Single-crystal X-ray structural analysis clearly shows that compound **1** consists of an α-$[SiW_{11}O_{39}]^{8-}$ framework on which are grafted two equivalent $PhCH_2P(O)$ groups through P–O–W bridges (see figure 1).

Table 1. Summary of crystallography data for compound **1**.

Empirical formula	$C_{62}H_{121}N_3O_{41}P_2SiW_{11}$
Formula weight	3677.00
Crystal size (mm^3)	$0.52 \times 0.32 \times 0.24$
Temperature (K)	293 (2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å, °)	$a = 14.386$ (3), $\alpha = 90$ $b = 27.015$ (5), $\beta = 91.44$ (3) $c = 25.480$ (5), $\gamma = 90$
Volume ($Å^3$)	9899 (3)
Z	4
Density ($Mg\,m^{-3}$)	2.467
Absorption coefficient (mm^{-1})	12.846
$F(000)$	6800
θ range (°)	1.51 to 22.99
Limiting indices	$-15 \le h \le 1$, $-1 \le k \le 29$, $-27 \le l \le 27$
Reflections collected	16,900
Independent reflections	13,713 ($R_{int} = 0.0298$)
Absorption correction	Empirical
Max. and min. transmission	0.326 and 0.218
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	13713/450/1064
Goodness-of-fit on F^2	1.032
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0638$, $wR_2 = 0.1364$
R indices (all data)	$R_1 = 0.1303$, $wR_2 = 0.1537$
Extinction coefficient	0.000111 (3)
Largest diff. peak and hole ($e\,Å^{-3}$)	3.009 and −2.924

3.2. *Infrared spectrum*

The highest wavenumbers ($1155\,cm^{-1}$) are assigned to the stretching vibrations of the P–C bond of organophosphorus unit, the peaks at 916, 977, 891, 813 and $732\,cm^{-1}$ are attributed to $Si–O_a$, $W–O_d$, $W–O_b–W$ and $W–O_c–W$ asymmetric stretching vibrational peaks for heteropolyanions with the Keggin structure, suggesting that the polyoxometallic moiety of compound **1** still retains the basic framework of the Keggin structure. However, perturbed by organophosphoryl groups, the stretching vibrational bands $\nu_{as}(W–O_b–W)$ and $\nu_{as}(W–O_d)$ are shifted to higher frequency compared to those of the starting α-$[SiW_{11}O_{39}]^{8-}$ anion [13]. Obviously, the increase of $\nu_{as}(W–O_b–W)$ and $\nu_{as}(W–O_d)$ is due to the decrease of negative charge on the polyanion through the fixation of organophosphoryl groups.

3.3. *^{31}P NMR spectrum*

The attachment of organophosphoryl groups onto the polyoxotungstate surface is also demonstrated by the resonance in the ^{31}P NMR. Compound **1** in CD_3CN displays a single, sharp resonance at 25.9, in lower field by comparison with that of $PhCH_2PO(OH)_2$ (δ 29.2) (see figure 2).

A heteropolyanion with a Keggin structure becomes the C_s lacunary polyanion α-$[X^{n+}W_{11}O_{39}]^{(12-n)-}$ 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 3a). When two double-bonded

Table 2. Selected bond lengths (Å) and angles (°) of **1**.

W(1)–O(27)	1.649(10)	W(1)–O(41)	1.917(10)
W(1)–O(18)	1.871(10)	W(1)–O(24)	1.998(11)
W(1)–O(10)	1.901(9)	W(1)–O(16)	2.336(10)
W(2)–O(4)	1.673(11)	W(2)–O(19)	1.903(9)
W(2)–O(36)	1.865(8)	W(2)–O(13)	1.960(10)
W(2)–O(29)	1.879(11)	W(2)–O(35)	2.357(10)
W(3)–O(7)	1.679(10)	W(3)–O(33)	1.910(9)
W(3)–O(23)	1.857(10)	W(3)–O(2)	1.969(11)
W(3)–O(9)	1.887(8)	W(3)–O(8)	2.216(9)
W(4)–O(3)	1.641(9)	W(4)–O(9)	1.947(8)
W(4)–O(40)	1.860(10)	W(4)–O(6)	1.998(10)
W(4)–O(41)	1.877(10)	W(4)–O(8)	2.190(9)
W(5)–O(22)	1.682(11)	W(5)–O(38)	1.872(10)
W(5)–O(37)	1.848(9)	W(5)–O(29)	1.912(11)
W(5)–O(32)	1.855(8)	W(5)–O(35)	2.423(10)
W(6)–O(5)	1.722(10)	W(6)–O(10)	1.909(9)
W(6)–O(20)	1.868(9)	W(6)–O(28)	1.916(10)
W(6)–O(23)	1.908(10)	W(6)–O(16)	2.316(10)
W(7)–O(31)	1.645(9)	W(7)–O(1)	1.967(10)
W(7)–O(18)	1.940(11)	W(7)–O(11)	1.981(10)
W(7)–O(40)	1.953(11)	W(7)–O(34)	2.345(8)
W(8)–O(21)	1.679(11)	W(8)–O(38)	1.907(9)
W(8)–O(24)	1.858(10)	W(8)–O(39)	1.926(10)
W(8)–O(28)	1.876(10)	W(8)–O(16)	2.342(11)
W(9)–O(26)	1.669(10)	W(9)–O(32)	1.895(9)
W(9)–O(11)	1.845(8)	W(9)–O(25)	1.934(11)
W(9)–O(39)	1.882(11)	W(9)–O(34)	2.393(10)
W(10)–O(17)	1.663(10)	W(10)–O(36)	1.898(8)
W(10)–O(25)	1.838(10)	W(10)–O(15)	1.959(10)
W(10)–O(1)	1.895(9)	W(10)–O(34)	2.346(10)
W(11)–O(30)	1.696(8)	W(11)–O(19)	1.947(11)
W(11)–O(33)	1.896(10)	W(11)–O(37)	1.967(11)
W(11)–O(20)	1.927(10)	W(11)–O(35)	2.348(8)
Si(1)–O(35)	1.584(9)	Si(1)–O(8)	1.663(11)
Si(1)–O(34)	1.614(9)	Si(1)–O(16)	1.677(12)
P(1)–O(12)	1.514(12)	P(1)–O(2)	1.566(11)
P(1)–O(13)	1.524(11)	P(1)–C(27)	1.815(13)
P(2)–O(14)	1.512(11)	P(2)–O(15)	1.532(11)
P(2)–O(6)	1.527(10)	P(2)–C(17)	1.786(12)
O(35)–Si(1)–O(34)	112.6(5)	O(35)–Si(1)–O(16)	107.4(5)
O(35)–Si(1)–O(8)	111.5(5)	O(34)–Si(1)–O(16)	108.1(5)
O(34)–Si(1)–O(8)	111.8(5)	O(8)–Si(1)–O(16)	104.9(5)
O(12)–P(1)–O(13)	112.2(6)	O(12)–P(1)–C(27)	109.6(7)
O(12)–P(1)–O(2)	110.7(6)	O(13)–P(1)–C(27)	105.5(7)
O(13)–P(1)–O(2)	110.7(6)	O(2)–P(1)–C(27)	108.0(6)
O(14)–P(2)–O(6)	110.8(6)	O(14)–P(2)–C(17)	109.7(7)
O(14)–P(2)–O(15)	110.9(6)	O(6)–P(2)–C(17)	110.6(6)
O(6)–P(2)–O(15)	111.2(6)	O(15)–P(2)–C(17)	103.4(6)

phosphoryl groups each bridge two of the five oxygen atoms that define the hole in the lacunary polyanion, the groups can bridge the oxygens such that they are either inequivalent or equivalent. The single resonance in the ^{31}P NMR spectrum indicates that the mode of attachment of the organic groups to the lacunary anion is equivalent, i.e. each organic group is connected to two oxygen atoms belonging to a triad and a diad, respectively (see figure 3b).

Synthesis of organic–inorganic hybrid α-$[Bu_4N]_3H[PhCH_2P(O)]_2SiW_{11}O_{39}$ **(1)** has been performed by reacting $PhCH_2PO(OH)_2$ with lacunary polyoxotungstate

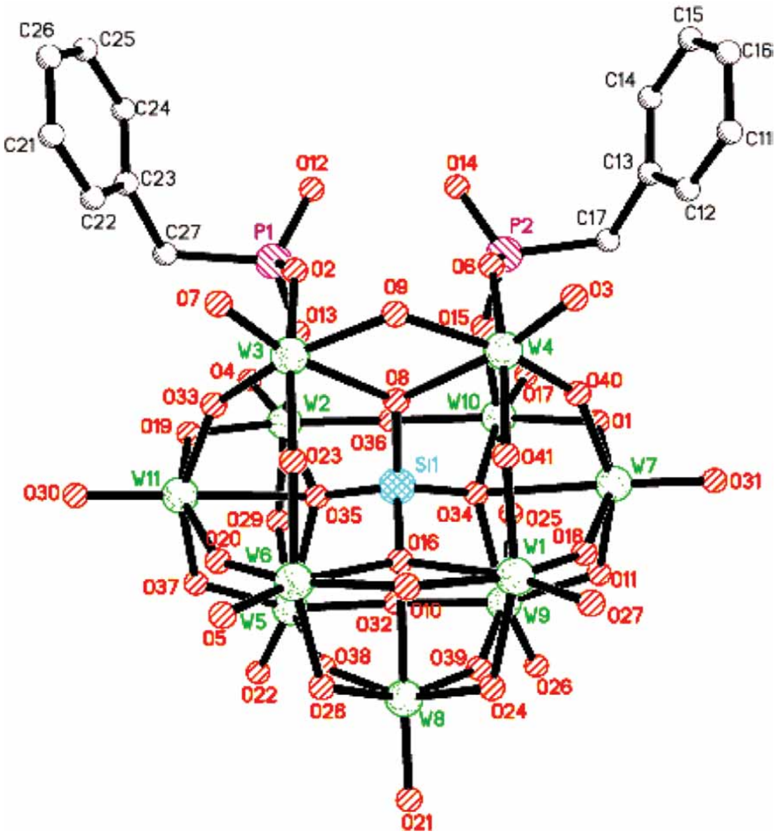


Figure 1. Molecular structure unit with atomic labeling for α-[$PhCH_2P(O)$]$_2SiW_{11}O_{39}^{4-}$.

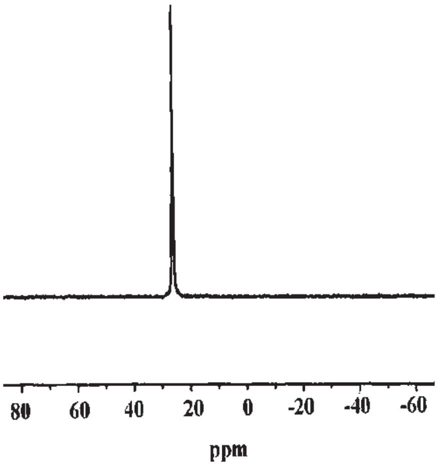
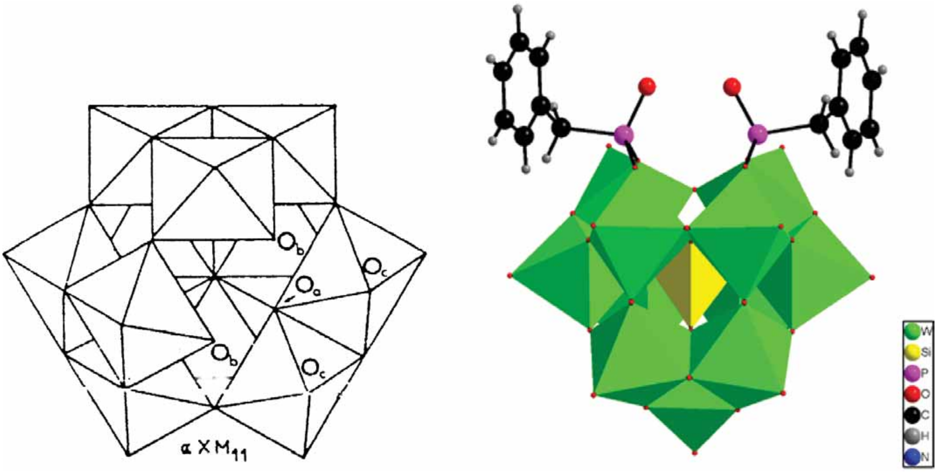


Figure 2. ^{31}P NMR spectrum of α-[$PhCH_2P(O)$]$_2SiW_{11}O_{39}^{4-}$ in CD_3CN.



(a) (b)

Figure 3. Polyhedral and ball-stick representation of (a) α-$[SiW_{11}O_{39}]^{8-}$ and (b) α-$[PhCH_2P(O)]_2SiW_{11}O_{39}^{4-}$. Each octahedron denotes WO_6, and the central tetrahedron denotes SiO_4.

α-$[Bu_4N]_4KH_3SiW_{11}O_{39}$ in acetonitrile, and a good crystal for X-ray diffraction study was successfully obtained. Elemental analysis results are consistent with the formulation of the title compound. The over reaction is

$$\alpha\text{-}[SiW_{11}O_{39}]^{8-} + 2PhCH_2PO(OH)_2 + 4H^+ \xrightarrow{MeCN} \alpha\text{-}[PhCH_2P(O)]_2SiW_{11}O_{39}^{4-} + 4H_2O$$

The single resonance in the ^{31}P NMR spectrum, which is in good agreement with single-crystal X-ray structural analysis, indicates that the mode of attachment of the organic groups to the lacunary anion is equivalent, i.e. each organic group is connected to two oxygen atoms belonging to a triad and a diad, respectively. The new hybrid anion still retained the basic Keggin structure.

Supplementary material

Crystallographic data for the structure of compound **1** reported in this article has been deposited in the Cambridge Crystallographic Data center as supplementary publication number CCDC 267266. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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