

三缺位 Keggin 结构磷钨酸甲基苯基硅衍生物 [(C₄H₉)₄N]₃[α -A-PW₉O₃₄(C₆H₅SiCH₃)₃]的合成和表征

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摘要: 通过三缺位 Keggin 结构杂多阴离子[α -A-PW₉O₃₄]⁹⁻和二氯甲基苯基硅烷在乙腈溶液中反应, 合成了一例结构新颖的甲基苯基硅衍生物[(C₄H₉)₄N]₃[α -A-PW₉O₃₄(C₆H₅SiCH₃)₃] (**1**), 并对其进行了元素分析, 红外光谱, 紫外光谱, 热分析和 X-射线单晶衍射等表征。该配合物属于三方晶系, 空间群为 *R*3*m*, 晶胞参数: *a*=2.261 3(2) nm, *b*=2.261 3(2) nm, *c*=1.797 6(4) nm, *V*=7.960 2(18) nm³, *Z*=3。在配合物中, 阴离子[α -A-PW₉O₃₄(C₆H₅SiCH₃)₃]³⁻呈 C_{3v} 对称, 3 个甲基苯基硅基团连接在三缺位的阴离子[α -A-PW₉O₃₄]⁹⁻表面, 整个阴离子显示“开放结构”。

关键词: 有机硅; 三缺位磷钨酸盐; 晶体结构; 合成

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A Methylphenylsilyl Group-Substituted Derivative Based on the Trivacant Keggin Structure Tungstophosphate [(C₄H₉)₄N]₃[α -A-PW₉O₃₄(C₆H₅SiCH₃)₃]: Synthesis and Structural Characterization

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Abstract: A methylphenylsilyl group-substituted derivative [(C₄H₉)₄N]₃[α -A-PW₉O₃₄(C₆H₅SiCH₃)₃] (**1**) has been obtained by reaction of the trivacant [α -A-PW₉O₃₄]⁹⁻ anion with dichloromethylphenylsilane C₆H₅SiCH₃Cl₂ in acetonitrile. The new complex was characterized by elemental analysis, IR spectra, UV spectra, thermogravimetric analysis and X-ray crystallography. The compound **1** crystallizes in the trigonal space group *R*3*m*, with lattice constants *a*=2.261 3(2) nm, *b*=2.261 3(2) nm, *c*=1.797 6(4) nm, *V*=7.960 2(18) nm³, and *Z*=3. The polyoxoanion [α -A-PW₉O₃₄(C₆H₅SiCH₃)₃]³⁻ has a structure of virtual C_{3v} symmetry with three C₆H₅SiCH₃ groups grafted on the surface of the trivacant tungstophosphate and displays an “open-structure”. CCDC: 830334.

Key words: organosilyl; trivacant tungstophosphate; crystal structure; synthesis

The design and synthesis of derivatized polyoxo-metalates (POMs) have attracted considerable attention in recent years originating from the fundamental interest of modeling catalysis by metal oxides as well as potential applications in different fields, including

bifunctional catalysis, antiviral and antitumoral chemotherapy^[1-2]. It is known that covalent attachment of organic or organometallic groups to POMs can be a strategy for increasing the structural diversity and improving their properties^[3-7]. This approach has been

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very successful for the synthesis of organic-inorganic hybrid POMs and a large number of such POMs have been synthesized and characterized in solution or in solid state since the pioneering work of Klemperer et al.^[8].

To date, there are three main types available in the literature regarding organometallic groups, namely organostannyl derivatives^[9-15], organophosphoryl^[16-20] and organosilyl derivatives^[21-32], also, there are a few of organonoblemetallic derivatives^[33-35] reported in the latest years. Among them, organosilyl derivatives are of particular interest and have been investigated for a long time probably because the isolated organosilyl groups can be easily incorporated into mono-, di-, or trivacant POMs. In 1979, the group of Knoth obtained the first organosilyl derivative $[\alpha-SiW_{11}O_{39}\{O(SiR)_2\}]^{4-}$ ($R = C_2H_5, C_6H_5, NC(CH_2)_3, C_3H_5$) by reaction of trichloro organosilanes with lacunary precursor $[\alpha-SiW_{11}O_{39}]^{8-}$ ^[24]. In particular, Thouvenot and co-workers studied this system deeply, and have reported a series of organosilyl derivatives, such as $[\alpha_2-P_2W_{17}O_{61}(RSi)_2O]^{6-}$ ^[25], $[(\gamma-SiW_{10}O_{36})(RSi)_2O]^{4-}$ ^[27], $[(\gamma-SiW_{10}O_{36})(RSiO)_4]^{4-}$ ^[27], $\alpha-A-[PW_9O_{34}(tBuSiO)_3(RSi)]^{3-}$ ^[28], $\alpha-B-[AsW_9O_{33}(tBuSiO)_3(HSi)]^{3-}$ ^[28], $[(\alpha-PW_{10}O_{36})(tBuSiOH)_2]^{3-}$ ^[29], and $\alpha-A-[PW_9O_{34}(tBuSiO)_3(SiR)]^{3-}$ ^[32]. Several years ago we reported on two new monoorganosilyl group-substituted organosilyl derivatives, $\alpha-A-[N^tBu_4]_3[PW_9O_{34}(RSiO)_3(RSi)]$ ($R = C_2H_5, CH_3$)^[30]. However, in marked contrast to the extensive reports of monoorganosilyl derivatives aforementioned, few diorganosilyl group-substituted organosilyl derivatives are known. Therefore, we decided to investigate the interaction of diorganosilyl groups with trivacant heteropolytungstates in some detail. Herein we report on the synthesis, single-crystal X-ray structure of $[(C_4H_9)_4N]_3[\alpha-A-PW_9O_{34}(C_6H_5SiCH_3)_3]$ (**1**), which represents the first polyoxoanion-based diorganosilyl group-substituted organosilyl derivative.

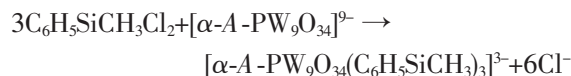
1 Experimental

1.1 Synthesis of $[(C_4H_9)_4N]_3[\alpha-A-PW_9O_{34}(C_6H_5SiCH_3)_3]$

Compound **1** can be synthesized as follows: $Na_9[\alpha-A-PW_9O_{34}] \cdot nH_2O$ (1.95 g, 0.80 mmol)^[36] and

N^tBu_4Br (0.78 g, 2.42 mmol) were suspended in 50 mL of CH_3CN and then $C_6H_5SiCH_3Cl_2$ (0.62 g, 3.25 mmol) was added dropwise under vigorous stirring. This solution was refluxed for 24 h and filtered. And then the resulting solution was allowed to evaporate slowly at room temperature. Colorless block crystals of **1** suitable for X-ray crystallography were obtained after several days. Yield: ca. 30% (Based on $Na_9[A-PW_9O_{34}] \cdot nH_2O$). Anal. Calcd. for $C_{69}H_{132}N_3O_{34}PSi_3W_9$ (%): C, 24.98; H, 4.01; N, 1.27; P, 0.93; Si, 2.54; W, 49.87. Found(%): C, 24.88; H, 4.00; N, 1.10; P, 1.01; Si, 2.57; W, 49.97.

Similar to $[\alpha-A-PW_9O_{34}(tBuSiO)_3(RSi)]^{3-}$ ^[28], the formation for **1** can be written as follow:



1.2 X-ray crystallography

Intensity data for **1** were collected at 296 K on a Bruker Apex II diffractometer using the graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.071\ 073$ nm). The structure was solved by combination of SHELXS-97 (direct methods) and SHELXH-97 (Fourier and least-squares refinement)^[37]. Lorentz polarization and Multi-scan absorption corrections were applied. All non hydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbon atoms were geometrically placed. All hydrogen atoms were refined isotropically as a riding mode using the default SHELXTL parameters. Crystallographic data and structure refinements for **1** are summarized in Table 1.

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1.3 Characterization

Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C elemental analyzer. ICP analyses were performed on a Perkin-Elmer Optima 2000 ICP-OES spectrometer. IR spectra were obtained on a Nicolet 170 SXFT-IR spectrometer using the technique of pressed KBr pellets in the range $400 \sim 4\ 000\ cm^{-1}$. XRPD were recorded on a Philips X'Pert-MPD instrument with Cu $K\alpha$ radiation ($\lambda = 0.154\ 056$ nm) in the range $2\theta = 10^\circ \sim 40^\circ$ at 293 K. TG analyses were carried out under N_2 atmosphere on a Mettler-Toledo TGA/SDTA 851^e instrument with the

Table 1 Crystallographic data and structural refinements for **1**

Empirical formula	C ₆₉ H ₁₃₂ N ₃ O ₃₄ PSi ₃ W ₉	<i>V</i> / nm ³	7.960 2(18)
Formula weight	3 317.67	<i>Z</i>	3
<i>T</i> / K	293(2)	<i>D_c</i> / (g·cm ⁻³)	2.076
Space group	<i>R</i> 3 <i>m</i>	<i>μ</i> / mm ⁻¹	9.828
Crystal system	Trigonal	Limiting indices	-26 ≤ <i>h</i> ≤ 26, -26 ≤ <i>k</i> ≤ 26, -21 ≤ <i>l</i> ≤ 21
<i>a</i> / nm	2.261 3(2)	Measured reflections	18 613
<i>b</i> / nm	2.261 3(2)	Independent reflections	3 342
<i>c</i> / nm	1.797 6(4)	<i>R</i> _{int}	0.036 7
<i>α</i> / (°)	90	Data / restraints / parameters	3 342 / 164 / 211
<i>β</i> / (°)	90	<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.036 5, 0.101 0
<i>γ</i> / (°)	120	<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.044 5, 0.107 9

heating rate of 10 °C·min⁻¹ from 25 to 800 °C. UV-Vis absorption spectra were obtained with a U-4100 spectrometer (distilled water as solvent) at 300 K.

2 Results and discussion

2.1 Crystal structure

Single crystal X-ray diffraction reveals that **1** crystallizes in the trigonal space group *R*3*m*. The molecular structure of **1** is composed of one [α-*A*-PW₉O₃₄(C₆H₅SiCH₃)₃]³⁻ polyoxoanions and three [(C₄H₉)₄N]⁺ cations (Fig.1). As shown in Fig.1a, the polyoxoanion [α-*A*-PW₉O₃₄(C₆H₅SiCH₃)₃]³⁻ consists of a [α-*A*-PW₉O₃₄]⁹⁻ framework with three equivalent C₆H₅SiCH₃ groups, and each C₆H₅SiCH₃ group is grafted onto this polyoxoanion by two Si-O-W bridges. Different from the close cage structure of α-*A*-[NⁿBu₄]₃[PW₉O₃₄(RSiO)₃](RSi) (R=C₂H₅, CH₃)^[30], the polyoxoanion [α-*A*-PW₉O₃₄(C₆H₅SiCH₃)₃]³⁻ displays an open structure while keeping the geometry of the parent trivacant polyoxoanion [α-*A*-PW₉O₃₄]⁹⁻. As we know, the POM-based organosilyl derivatives previously reported are limited and mainly

confined to monoorganosilyl group-substituted species. There is still no report about diorganosilyl analogue. Consequently, the most remarkable structural feature of **1** is that it is the first trivacant tungstophosphate-based example of diorganosilyl group-substituted organosilyl derivative in which the Si atom is connected to two organic groups. There are minor disorder in the ligand with C2, C3, C4/C4', C5, C6, C7/C7' in **1** which lie about an inversion centre.

Compared to the saturated Keggin structure, the P heteroatom adopts a slightly distorted tetrahedral geometry coordinated by oxygen atoms with an average P-O bond length of 0.153 3(12) nm, which is ascribed to the removal of three corner-shared WO₆ octahedra and the incorporation of three C₆H₅SiCH₃ groups. Fig.1b shows that the incorporated silicon atoms are defined by two O atoms from [α-*A*-PW₉O₃₄]⁹⁻ moieties with average bond lengths 0.162 6(9) nm and two carbon atoms from the methyl and phenyl, respectively. This coordination mode is similar to Sn atoms of [(Sn(CH₃)₂)₄(H₂P₄W₂₄O₉₂)₂]²⁸⁻^[15], Si atoms as

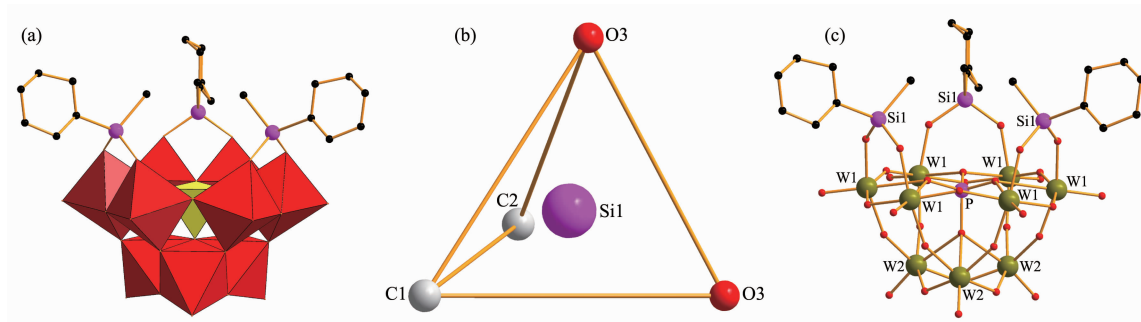


Fig.1 (a) Polyhedral and ball-and-stick representation of the polyoxoanion in **1**; (b) Coordination environment of Si atom in **1**; (c) Ball-and-stick representation of the polyoxoanion in **1**

well as Sn atoms are bound to two organic groups. Although there has been such organotin derivative, still has no any similar report for POM-based diorganosilyl group-substituted organosilyl derivative. To our knowledge, **1** is the first example of POM-based diorganosilyl group-substituted organosilyl derivative. Packing arrangement viewed down c axis of the polyoxoanion in **1** is illustrated in Fig.2. The infinite hexa-number rings are formed via π - π and electrostatic interactions with one polyoxoanion locating in the center of the ring.

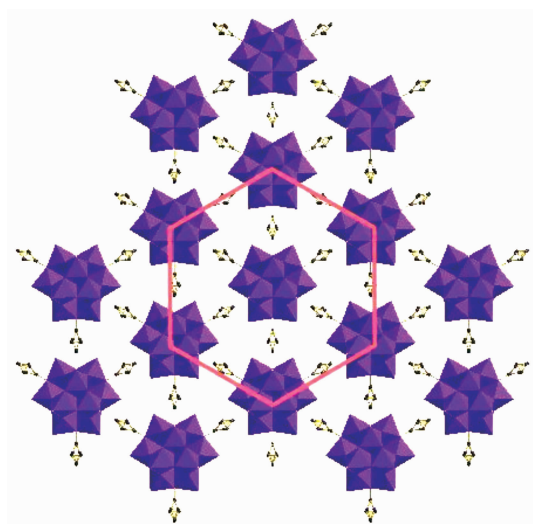


Fig.2 Packing arrangement viewed down the c axis

2.2 FT-IR spectra

The IR spectrum of **1** (Fig.3) is very similar to that of $Na_9[\alpha-A-PW_9O_{34}] \cdot nH_2O$, which is indicative of the retention of the $[\alpha-A-PW_9O_{34}]^{9-}$ framework. In the low-wavenumber region, characteristic vibration patterns derived from the Keggin frameworks are observed. Four characteristic vibration bands assigned

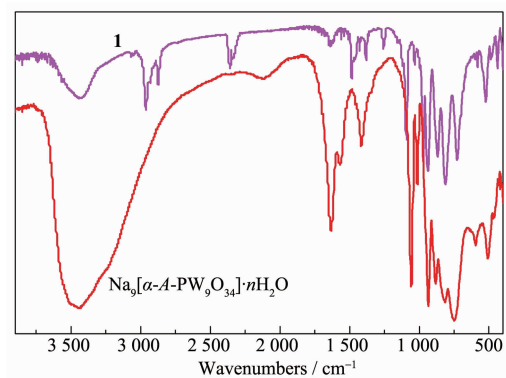


Fig.3 Infrared spectra of **1** and $Na_9[\alpha-A-PW_9O_{34}] \cdot nH_2O$

to $\nu(W-O_t)$, $\nu(P-O_a)$, $\nu(W-O_b)$ and $\nu(W-O_c)$ appear at 974 and 938, 1 088 and 1 028, 872, and 812 cm^{-1} for **1**, respectively. Additionally, the stretching bands of $-CH_3$ and $-C_6H_5$ have been typically observed at 2 874 \sim 2 961 and 3 040 \sim 3 072 cm^{-1} , respectively. The bands at wide 3 420 and strong 1 625 cm^{-1} are attributed to the lattice water and ligand water molecules. As above mentioned, the results of IR spectrum are well identical with those of X-ray diffraction structural analysis.

2.3 UV-Vis spectrum

The UV-Vis spectrum (Fig.4) of **1** displays a strong absorption at 260 nm and a weak peak at near 191 nm, which are associated with the charge-transfer bands corresponding to $O_t \rightarrow W$ and $O_{b(c)} \rightarrow W$, respectively.

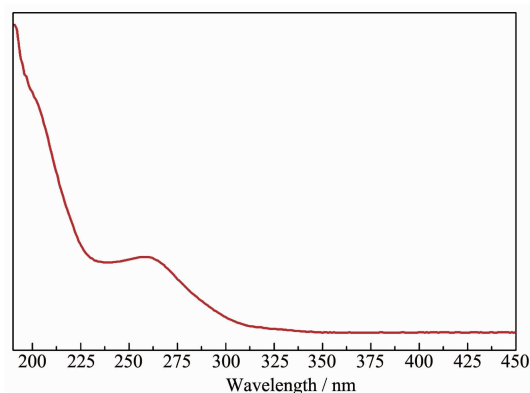


Fig.4 UV-Vis spectrum for compound **1** in aqueous solution

2.4 TG analyses

The thermal gravimetric curve of **1** (Fig.5) indicates two steps of weight loss, giving a total weight loss of 30.63% in the range of 25 \sim 850 $^{\circ}C$, accordant with the calculated loss of 29.28%. The

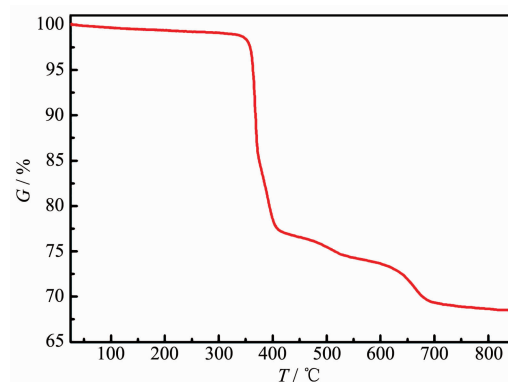


Fig.5 TG curve of **1**

first stage from 25 to 412 °C is attributed to the removal of three organic ammonium molecules, and the observed weight loss 22.40% is consistent with the calculated value 21.93%. The second stage with the weight loss of 8.23% occurs between 412 and 800 °C, which may be assigned to the loss of three methyl and three phenyl (calcd. 7.35%).

2.5 XRPD patterns

The experimental XRPD pattern of the bulk product of **1** is in good agreement with the simulated one that are based on the results from single-crystal XRD, which indicates the phase purity of the sample (Fig.6). The different intensities of the experimental and simulated XRPD patterns are due to the variation in the preferred orientation of the powder sample during data collection.

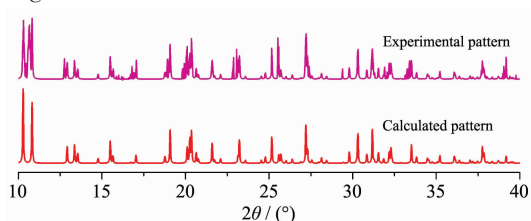


Fig.6 Experimental and simulated XRPD patterns of **1**

3 Conclusions

In summary, we have successfully incorporated diorganosilyl groups into a trivacant Keggin-type tungstophosphate. The title compound is the first example of POM-based diorganosilyl group-substituted organosilyl derivative. Further, the successful synthesis of **1** may provide possibilities for designing new diorganosilyl group-substituted organosilyl derivatives.

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