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Mono- and Di-Sc-Substituted Keggin Polyoxometalates: Effective Lewis Acid Catalysts for Nerve Agent Simulant Hydrolysis and Mechanistic Insights

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ABSTRACT: Recently, the hydrolysis of nerve agents by Lewis acid catalysts has attracted considerable attention. The development of molecular catalysts, such as polyoxometalates (POMs) with Lewis acidic sites, is helpful to improve degradation efficiency and understand the catalytic mechanism at a molecular level. Herein, two novel Keggin-type POMs, namely, mono-Sc-substituted K₄[Sc(H₂O)PW₁₁O₃₉]·22H₂O·2(CH₃COOK) (1) and di-Sc-substituted Na₇[Sc₂(CH₃COO)₂PW₁₀O₃₈]·10H₂O·2CH₃COONa (2), have been successfully synthesized and thoroughly characterized by routine techniques. To our knowledge, 1 and 2 represent the first example of discrete Sc-substituted Keggin clusters. Compared with the reported Sc-containing POMs, 1 and 2 exhibit relatively good solubility and stability in aqueous solution, as evidenced by ³¹P nuclear magnetic resonance spectroscopy and Fourier-transform infrared spectroscopy. The two Sc-substituted POMs can



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effectively catalyze the hydrolytic decontamination of dimethyl 4-nitrophenyl phosphate (DMNP), a nerve agent simulant, at nearneutral pH. Notably, the catalytic performance of 2 (conversion: 97%) is much better than that of 1 (conversion: 28%). It is found that the different coordination environment of Sc is the key factor to impact their activity. Mechanistic studies including the control experiments and spectroscopy analysis (13 C nuclear magnetic resonance spectroscopy and electrospray ionization mass spectrometry) show that under the turnover conditions the coordinated acetate dissociates from 2 and the exposed coordinatively unsaturated Sc center is more active than the water-coordinated Sc in 1 for binding with DMNP.

1. INTRODUCTION

Chemical warfare agents (CWAs) are highly toxic chemicals, which represent a significant threat to both military and civilian populations.¹ Therefore, rapid transformation of CWAs to nontoxic products is an urgent issue. Among CWAs, nerve agents and vesicants are used more commonly. Nerve agents are organophosphorus esters containing P-X bonds (X = F, CN, SR) that cause a range of incapacitating states by inactivating acetylcholinesterase and even death in high doses. Hydrolysis is a primary and effective way to decontaminate nerve agents. Most nerve agents, such as Sarin and Soman, can be quickly decomposed in strong alkali solution. Recently, the hydrolysis catalyzed by Lewis acid catalysts has attracted increasing attention. Since Lewis acidic sites are available to bind nerve agents and activate the phosphorus oxygen bond, the hydrolysis rate is significantly increased. A series of Zrbased hydrolytic catalysts including metal oxides,³ metal hydroxides,⁴ and metal-organic frameworks (MOFs)⁵⁻⁷ have been reported, but due to their heterogeneous nature, it is difficult to determine the exact structure of active sites. Therefore, developing molecular catalysts with Lewis acidic centers contributes to understanding the hydrolytic mechanism and governing factors during the decontamination process.

Polyoxometalates (POMs) are a large class of nanosized metal–oxygen clusters formed by Mo, W, V, Nb, and Ta with oxo ligands.^{8–11} POMs combine the composition/structure tunability of molecular catalysts and the stability of heterogeneous catalysts, exhibiting remarkable catalytic performance in a range of oxidation, esterification, and hydrolysis reactions. In addition, some strong Lewis acidic metal centers, such as Zr(IV), Ce(IV), and Ti(IV), can be incorporated into the skeleton of POMs by using lacunary POMs as ligands. Previous studies show that some POMs are active for the decontamination of CWAs and/or their simulants. For example, $\{PV_2Mo_{10}O_{40}\},^{12-15}$ K₂H[Co(H₂O)₄]-[AsMo₆O₂₁(Ala)(PHBA)₂],¹⁶ {PNb₁₂O₄₀(VO)₂·(V₄O₁₂)₂},¹⁷ and Fe-containing and Ni-substituted polyoxotungstates^{18–22} can catalyze the oxidative decontamination of sulfur mustard or its simulants, while polyoxoniobates, including {Nb₆O₁₉},

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Scheme 1. Synthesis and Structures of 1 and 2^{a}



^aRed polyhedra, WO₆; yellow polyhedral, PO₄. In the polyhedral representation of 1, the disordered atoms were omitted or simplified for clarity.

 $\rm K_{12}[Ti_2O_2][GeNb_{12}O_{40}]$ and $\rm \{Nb_{47}O_{128}(OH)_6(CO_3)_2\}$, are effective catalysts for the basic hydrolysis of CWAs.^{23-25} Recently, Zr-substituted POM, $\{[\alpha\text{-PW}_{11}O_{39}Zr(\mu\text{-OH})-(H_2O)]_2\}$, was used to catalyze the hydrolysis of nerve agent and/or its simulants in a buffered solution or at the gas–solid interface.^{26,27} However, the used Zr-POM dimer is unstable, and it dissociates into monomeric form under the turnover conditions.

Sc(III)-containing complexes and materials have been used as Lewis acid catalysts for some important organic reactions. Recently, 3d Sc(III) ion has been successfully introduced into POMs. Compared with the other 3d transition metals containing POMs, the structures of Sc-containing POMs are very limited probably due to their crystallization challenge. In 2012, Niu et al. reported the first case of Sc-containing POM, which is a two-dimensional hybrid based on $\{[(\alpha-SiW_{11}O_{39})-Sc(H_2O)]_2(C_2O_4)\}^{12-.28}$ After that, $[Sc_4(H_2O)_{10}(B-\beta-SbW_9O_{33})_2]^{6-}$, $[Sc_6Sb_2W_6O_{19}(H_2O)_6(SbW_9O_{33})_6]^{31-}$, and $[Sc_{11}W_6O_{20}(OH)_2(H_2O)_{16}(SbW_9O_{33})_6]^{27-}$ were subsequently synthesized in Zheng's group by using $\{B-\alpha-SbW_9O_{33}\}$ as building blocks.^{29,30} The reported Sc-containing POMs have poor solubility in aqueous solution, and thereby, their solution behavior and homogeneous catalytic activity are nearly unexplored.

In this work, we present the synthesis and structures of two novel Sc-substituted Keggin-type heteropolytungstates, $[Sc-(H_2O)PW_{11}O_{39}]^{4-}$ (1) and $[Sc_2(CH_3COO)_2PW_{10}O_{38}]^{7-}$ (2), where the substituted Sc centers exhibit different coordination environments (Scheme 1). Since the two Sc-substituted POMs have good solubility and stability in aqueous solution, we explored their hydrolysis activities toward dimethyl 4-nitrophenyl phosphate (DMNP), a Sarin simulant. 1 and 2 can effectively promote the degradation of DMNP at near-neutral pH. Interestingly, compound 2 is more active than 1, and on the basis of control experiments and spectroscopy analysis, a possible mechanism was proposed to explain the observed hydrolysis activity.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. The POM precursor, $Na_9[A-PW_9O_{34}]$ ·7H₂O, was prepared according to the literature method³¹ and identified by Fourier-transform infrared (FT-IR) spectroscopy. The other reagents were purchased from commercial sources and

used without further purification. Dimethyl 4-nitrophenyl phosphate (DMNP) were purchased from Alfa Aesar (China) Chemicals Co., Ltd.

Caution! The nerve agent simulant, DMNP, is highly toxic and must be handled only by trained personnel using applicable safety procedures in a closed system or a hood under good ventilation.

FT-IR spectra were recorded as the pressed KBr pellets on a Nicolet 170SX-FT/IR spectrometer in the range of 400-4000 cm⁻¹. Thermogravimetric analyses were performed on a TG-DTA 6200 device from room temperature to 800 $^\circ$ C with a heating rate of 10 $^\circ$ C min⁻¹ under nitrogen atmosphere. Elemental analyses (C, H, and N) were measured on an ElementarVario EL Cube Elmer CHN elemental analyzer; Sc and W were determined by inductively coupled plasma-mass spectrometry (ICP-MS) with a PerkinElmer NexlON 350X spectrometer. Power X-ray diffraction (PXRD) patterns were obtained using a Bruker D8 Advance X-ray diffractometer with Cu K α radiation (λ = 1.54 Å). The UV–visible spectra were recorded with a Shimadzu UV-3600 ultravisible spectroscopy instrument. Electrospray ionization mass spectrometry (ESI-MS) was obtained in the negative-ion mode using an Agilent Q-TOF 6520 LC/MS mass spectrometer. The electrospray ionization source conditions: V_{cap}, 3500 V; skimmer, 65 V; nebulizer, 30 psi; drying and nebulizer gas, N2; drying gas flow, 10 L/min; drying gas temperature, 300 °C; fragmentor, 80 V; scan range 100-2000 m/z. The sample solutions with the concentration of approximately 10^{-4} M were made and analyzed by direct injection using an automatic sampler with a flow rate of 0.2 mL/min. ³¹P nuclear magnetic resonance spectroscopy (³¹P NMR) spectra were performed on a Bruker 400 MHz instrument in D₂O or MeOD. ¹³C nuclear magnetic resonance spectroscopy (¹³C NMR) spectra were also determined on the Bruker 700 MHz instrument in D₂O.

2.2. Synthesis of K₄[Sc(H₂O)PW₁₁O₃₉]·22H₂O·2(CH₃COOK) (1). $Na_9[A-PW_9O_{34}]$ ·7H₂O (0.2564 g, 0.10 mmol) and Sc(NO₃)₃· nH_2O (0.0578 g, 0.20 mmol) were dissolved in 12 mL of NaAc/HAc buffer solution (0.3 M, pH 4.5). The above solution was stirred and kept at 70 °C for 3 h; then, the cloudy solution was cooled to room temperature, and a small amount of precipitate was removed by filtration. The pH value after the reaction is about 4.6. After that, KCl (0.100 g, 1.34 mmol) was added, and evaporation of the filtrate at room temperature resulted in colorless small block crystals of 1 after several weeks. The products were collected by filtration and air-dried (yield: 39% based on P). Compound 1 can also be prepared by using $K_7[\alpha$ -PW₁₁O₃₉]·14H₂O as staring materials. During the synthesis, we tried other pH values. There was no crystal formed when the pH was below 4.5 or above 5.0. In the pH range of 4.5-5.0, a small amount of compound 1 and a large amount of precipitate were obtained together. Selected IR (2% KBr pellet, ν/cm^{-1}): 3440(s), 1571(m), 1462(m), 1093(s), 1054(s), 959(m), 805(m), 511(w) cm⁻¹

Elemental analysis (%) calcd for 1: K 6.72, Sc 1.29, P 0.89, W 57.96, C 1.37; found: K 6.90, Sc 1.48, P 0.96, W 57.45, C 1.66.

2.3. Synthesis of Na₇[Sc₂(CH₃COO)₂PW₁₀O₃₈]·10H₂O· 2CH₃COONa (2). 2 was prepared by a procedure similar to that of 1, and the only difference is that 0.5 M NaAc/HAc buffer solution (pH = 5.5) was used instead of the 0.3 M buffer (pH = 4.5). The pH value after the reaction is about 5.7, and NaCl (0.100 g, 1.71 mmol) was added into the filtrate to promote crystallization. After several weeks of evaporation, colorless block single crystals of 2 were collected by filtration and air-dried (yield: 23% based on P). Compound 2 can only be prepared under pH 5.5. The experiments under other pH condition below or above 5.5 led to the formation of precipitate. In addition, compounds 1 and 2 were never seen together in the same batch. In addition, the preparation of 2 using $\left[\alpha\right]$ $PW_{11}O_{39}$ is unsuccessful. Selected IR (2% KBr pellet, ν/cm^{-1}): 3390(s), 1625(s), 1535(s), 1469(m), 1401(s), 1048(s), 950(s), 879(m), 802(w), 643(m) cm⁻¹. Elemental analysis (%) calcd for 2: Na 6.49, Sc 2.82, P 0.97, W 57.62, C 3.01; found: Na 6.50, Sc 2.94, P 0.95, W 57.20, C 2.68.

2.4. X-ray Crystallography. The intensity data of 1 and 2 were collected on a Bruker APEX 2 DUO CCD single-crystal diffractometer equipped with a sealed Mo tube and a graphite monochromator ($\lambda = 0.71073$ Å) at 120 K. The crystals were mounted in a Hampton cryoloop with oil to prevent the loss of crystal waters. Then, both structures were solved by direct methods and refined by the full-matrix least-squares method fitting on $(\Sigma w (|F_0|^2 - |$ $(F_c)^2)^2$) using the SHELXTL program package (Bruker).³²⁻³⁴ The H atoms of the crystal waters were not located, and all heavy atoms were refined with anisotropic thermal parameters. The crystal data and structure refinement details for the three compounds are summarized in Table S1, and the selected bond length and bond angles are given in Table S2. The crystallographic data have been deposited to the Cambridge Crystallographic Data Centre (CCDC) as entries CCDC 1991918 (1) and 1991919 (2). The final molecular formula of 1 and 2 were defined by single-crystal X-ray diffraction data combined with elemental analysis.

2.5. Hydrolysis of DMNP. First, the 0.5 M HAc/NaAc solution was prepared and the pH was adjusted to 7.0 by NaOH before the addition of POMs or other catalysts. According to the calculation, at pH 7.0 the ratio of HAc to NaAc is about 1:175 and acetate ions are the predominant species. In some experiments, deionized water was used instead of 0.5 M HAc/NaAc solution. For all hydrolysis experiments, the aqueous solution of POM catalyst (0.006 mmol, 0.4 mL) and DMNP methanol solution (0.02 mmol, 0.1 mL) were separately prepared, and their combination starts the reaction. The catalytic reaction was carried out at room temperature with stirring and was monitored by ³¹P NMR spectroscopy at various intervals of time. The conversion of DMNP was calculated according to the peak area ratio of the products to DMNP and the products.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Structure. As shown in Scheme 1, compounds 1 and 2 were synthesized by the conventional aqueous solution method using a trilacunary Keggin-type precursor, $Na_9[A-\alpha-PW_9O_{34}]$, and scandium nitrate as starting materials in a NaAc/HAc buffer solution. The structural transformation from $\{A-\alpha-PW_9O_{34}\}$ to monolacunary $\{\alpha$ - $PW_{11}O_{39}$ or dilacunary { α - $PW_{10}O_{38}$ } happens during the synthesis of the two Sc-substituted POMs, which has also been observed in literature reports.35 The control experiments indicate that the pH value and the concentration of NaAc/ HAc buffer play important roles in the synthesis of 1 and 2. Compound 1 was synthesized in 0.3 M NaAc/HAc buffer (pH 4.5), while compound 2 was isolated in 0.5 M NaAc/HAc buffer (pH 5.5). When the pH value or concentration of buffer were changed, only amorphous precipitates were obtained. We speculate that on one side the formation of lacunary POM subunit is sensitive to pH; on the other side, a high

concentration buffer, especially at higher pH (such as 5.5), would provide more acetate ions, facilitating its coordination with Sc.

Single-crystal X-ray diffraction analysis reveals that compound 1 crystallizes in the tetragonal space group I4/mmm. As shown in Scheme 1, 1 contains a mono-Sc-substituted Keggintype polyanion cluster, $[Sc(H_2O)PW_{11}O_{39}]^{4-}$, with $C_{3\nu}$ symmetry. The $[Sc(H_2O)PW_{11}O_{39}]^{4-}$ cluster can be viewed as incorporating a Sc ion into the classical monovacant Keggintype $[\alpha - PW_{11}O_{39}]^{7-}$. In this cluster, Sc ion coordinates with five O atoms from $[\alpha$ -PW₁₁O₃₉]⁷⁻ and one water molecule to exhibit a distorted octahedral geometry. Notably, both positional disorder and atomic occupancy disorder can be observed in the structure. The central P is surrounded by eight half-occupied oxygen atoms, and four metal centers are occupied by disordered Sc and W with an occupancy of 25% and 75%, respectively. Monosubstituted Keggin-type clusters are important members in the POM family, and many transition metals have been introduced into the lacunary site of $\{XW_{11}O_{39}\}^{.36-42}$ Compared with other 3d metal-substituted POMs, Sc-substituted Keggin-type POM has rarely been reported. In 2006, the mono-Sc-substituted Keggin was been detected by ³¹P NMR in the solution of Sc ion and $[PW_{11}O_{39}]^{7-}$. In addition, monosubstituted $[Sc(H_2O)-SiW_{11}O_{39}]^{4-}$ subunits were isolated in a 2D hybrid {[Cu- $(en)_{2}(H_{2}O)]_{2}[Cu(en)_{2}]_{2}[(\alpha-SiW_{11}O_{39})Sc(H_{2}O)]_{2}(C_{2}O_{4})]^{28}$ To our knowledge, compound 1 represents the first discrete mono-Sc-substituted Keggin cluster.

Compound 2 crystallizes in the triclinic space group $P\overline{1}$ and possesses a novel di-Sc-substituted cluster, $[Sc_2(CH_3COO)_2PW_{10}O_{38}]^{7-}$, with C_3 symmetry. After decomposition and recombination, the added $[A-\alpha-PW_9O_{34}]^{9-1}$ precursor was transformed to a rare disubstituted Keggin $[\alpha(1,8)$ -PW₁₀O₃₈]¹¹⁻ and the two vacant sites are occupied by two Sc ions (Scheme 1). In this polyanion, each Sc center is coordinated with five O atoms from lacunary polyanion $[\alpha(1,8)-\mathrm{PW}_{10}\mathrm{O}_{38}]^{11-}$ and two O atoms from one η^2 -acetate, exhibiting a monocapped trigonal prism geometry (Figure S2). The Sc–O bond lengths are in the range of 2.02(5)-2.44(1)Å. The polyanion can also be described as assembling two $\{W_3O_{13}\}$ triads and two $\{W_2O_{12}Sc(OAc)\}$ subunits around a central PO_4 tetrahedron, where the two Sc centers are separated without sharing any oxygen atom and where the Sc…Sc distance is 5.02 Å. As in 2, the coordinated water molecule of Sc is replaced by acetate, and the Sc ions in the two clusters exhibit different coordination environment, which might lead to different Lewis acid catalytic activity. Compared with monosubstituted and trisubstituted POMs, the examples of disubstituted POMs are limited. Several ditransition-metalsubstituted POMs based on $\{\alpha(1,8)-XW_{10}O_{38}\}$ (X = Ge, As) have been reported as subunits to construct dimeric, trimeric, or tetrameric POM clusters.^{43,44} To our knowledge, the discrete disubstituted POM based on Keggin { $\alpha(1,8)$ - $XW_{10}O_{38}$ remains largely unexplored.

3.2. Catalytic Hydrolysis of Nerve Agent Simulant. Compared with the reported insoluble Sc-containing POMs, the synthesized two Sc-substituted Keggin clusters show relatively good water solubility with the maximum solubility of about 0.02 mmol/L. Compound **1** is only soluble in water. In addition to water, compound **2** can also be dissolved in some polar organic solvents, such as MeOH, DMF, and DMSO. When **1** and **2** were recrystallized from the solution, no change was observed in their IR spectra (Figure S7), indicating that the two clusters remain stable in solution. Due to the good water solubility and the existence of Lewis acidic Sc centers in 1 and 2, the degradation of DMNP, a Sarin simulant, was selected to evaluate their hydrolytic activity (Scheme 2).

Scheme 2. Hydrolysis of DMNP by Sc-substituted POMs 1 and 2



Before the catalytic hydrolysis study, we test the pH dependence of compounds 1 and 2 monitored by ³¹P NMR (Figures 1 and S13). As shown in Figure 1a, only a single resonance is observed at -13.47 ppm at pH 3–8, meaning that 1 is stable in a wide pH range. Compound 2 remains stable at pH 6–8 with a single resonance at -8.89 ppm. When the pH decreases to 5, the decomposition of compound 2 happens, resulting in the coexistence of mono-Sc-substituted POM at -13.47 ppm and di-Sc-substituted POM at -8.89 ppm. With the increase of solution acidity, a single resonance is observed at -13.47 ppm, meaning that 2 completely converts to 1 at low pH values (Figure 1b).

Considering the stability of two Sc-substituted POM catalysts, the hydrolysis of DMNP was performed at nearneutral pH adjusted by HAc/NaAc solution. In a typical reaction, the POM catalyst (0.006 mmol) was dissolved in 0.5 M HAc/NaAc aqueous solution (0.5 mL) with a pH of 7, and then, the addition of DMNP (0.02 mmol) in MeOH (0.1 mL) started the reaction. The catalytic reaction was performed under ambient conditions. As shown in Table 1 entries 1 and 2, both compounds 1 and 2 are active for the hydrolytic decontamination of DMNP, i.e., 2 converts 97% of DMNP to nontoxic products in 9 h, while under the otherwise identical conditions 1 only gives a conversion of 28%. In the blank test, a negligible amount of DMNP is consumed (Table 1, entry 3). Under otherwise identical conditions, $Sc(NO_3)_3$ as a homogeneous catalyst with 5 equiv to Sc-substituted POM gives a conversion of 17% (Table 1, entry 4) and that with 2 equiv removes 11% of DNMP (Table 1, entry 5), which are far lower results than the conversion of compound 2 (97%). However, when HAc/NaAc solution was replaced by

deionized water, only a negligible DNMP is consumed by $Sc(NO_3)_3$ (Table 1, entry 6), indicating that the hydrolytic activity of $Sc(NO_3)_3$ greatly depends on the use of HAc/NaAc solution. In addition, the influence of lacunary Keggin POMs on the catalytic hydrolysis has been investigated. As in the 0.5 M HAc/NaAc system, the addition of monolacunary Keggin $K_7[\alpha$ -PW₁₁O₃₉] gave rise to a cloudy solution, so the hydrolysis reaction was performed in deionized water instead. Neither monolacunary Keggin $K_7[\alpha$ -PW₁₁O₃₉] (Table 1, entry 7) nor a simple mechanical mixture of $K_7[\alpha$ -PW₁₁O₃₉] and $Sc(NO_3)_3$ with a mole ratio of 1:2 (Table 1, entry 8) is active for the degradation of DMNP. The Sc-substituted POM precursor, Na₉[A-PW₉O₃₄], was nearly insoluble at room temperature, so we performed the hydrolysis experiment at 50 °C. Even though the hydrolysis reaction can be accelerated by heating, only a conversion of 12% is achieved by Nao A- PW_9O_{34}] (Table 1, entry 9). The above results indicate that the substituted Sc centers in POM are the active sites for the hydrolysis of nerve agent simulant. Without using HAc/NaAc to adjust the pH, DMNP can also be detoxified by 1 and 2 (Table 1, entries 10 and 11). However, after 6 h reaction we found that 2 was partially decomposed owing to the decrease of pH caused by the accumulation of acidic products (Figure S15). In contrast, catalysts 1 and 2 are basically stable in the presence of HAc/NaAc, confirmed by ³¹P NMR and IR spectra (Figures S12 and S16). Due to the good catalytic performance, the time profile for the hydrolytic decontamination of DMNP using 2 is presented in Figure 2.

Although both 1 and 2 contain Lewis acidic Sc centers, the hydrolysis rate of 2 is obviously higher than that of 1. Given that the substituted Sc ions content of 2 is double that of 1, the turnover frequency (TOF) calculated relative to the amount of Sc was used to evaluate their catalytic activity. Catalyst 1 with a TOF of 0.18 h^{-1} is still more active than ${\bf 2}$ with a TOF of 0.10 h^{-1} (TOF was calculated relative to the amount of Sc). To further verify the impact of Sc(III) amount on the DMNP hydrolysis, a control using a double dosage of 1 (0.012 mmol) was conducted. The double dosage of 1 led to the improvement of conversion in some degree, but it was still much lower than the conversion of 2 (Table S3). The special role of bimetallic Lewis-acidic metal centers has been reported in the hydrolytic decontamination catalyzed by Zr-containing MOFs and hydrolytic enzymes, where the two metal centers are bridged by a hydroxide group.⁷ Nevertheless, in 2 the two



Figure 1. ³¹P NMR of 6 mM compound 1 (a) and 2 (b) at varying pH values in deionized water. The pH values of the solutions were adjusted with HAc and NaOH (400 MHz NMR, 128 scans).

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Table 1. Decontamination of DMNP by Using Different Catalysts^a

entry	catalyst	conditions	time (h)	conv. (%)
1	compound 1	0.006 mmol, 0.5 M HAc/NaAc	9	28
2	compound 2	0.006 mmol, 0.5 M HAc/NaAc	9	97
3	blank	no catalyst, 0.5 M HAc/NaAc	9	trace
4	$Sc(NO_3)_3$	0.03 mmol, 0.5 M HAc/NaAc	9	17
5	$Sc(NO_3)_3$	0.012 mmol, 0.5 M HAc/NaAc	9	11
6	$Sc(NO_3)_3$	0.03 mmol, H ₂ O	9	trace
7	$K_7[\alpha - PW_{11}O_{39}]$	0.006 mmol, H ₂ O	9	trace
8	$K_7[\alpha - PW_{11}O_{39}] + Sc(NO_3)_3$	0.015 mmol + 0.03 mmol, H ₂ O	9	trace
9	Na ₉ [A-PW ₉ O ₃₄]	0.007 mmol, H ₂ O, 50 $^{\circ}$ C	7	12
10	compound 1	0.006 mmol, H ₂ O	6	22
11	compound 2	0.006 mmol, H ₂ O	6	86

"Reaction conditions: DMNP (0.02 mmol) in 0.1 mL of MeOH, catalyst in HAc/NaAc aqueous solution (0.5 M, 0.5 mL) with pH of 7 or 0.5 mL of deionized water. All the hydrolysis of DMNP was performed in a homogeneous system, entries 1-8, 10, and 11 at room temperature and entry 9 at 50 °C as Na₉[A-PW₉O₃₄] is insoluble at room temperature.



Figure 2. (a) The time profile for DMNP decontamination; (b) ³¹P NMR of DMNP decontamination catalyzed by 2 at various intervals of time.

Sc centers are connect by O–W–O and the Sc…Sc distance (5.02 Å) is much longer than the Zr…Zr distance (3.53 Å) in the MOFs. Therefore, the synergetic effect is not present in 2.

Since the number of Lewis acidic center in 1 and 2 is not the main factor to influence the hydrolysis of DNMP, we speculate that their different catalytic activity is possibly related to the different coordination environment of Sc. The Sc ion coordinates with a water molecular in 1, while it coordinates with an acetate in 2. Generally, the aqua ligand in POMs firmly combines with metal centers. In comparison, the dissociation of acetate ligand is relatively easy. To explore the coordination stability of acetate in the solution, we recorded the ¹³C NMR spectra of **2**. As shown in Figure 3, the C peaks of the methyl group with δ = 23.25 ppm and carboxyl group with δ = 181.53 ppm are observed in the aqueous solution of 2. When equivalent NaAc was added to above solution, the intensity of the two peaks was correspondingly increased but without observation of a new peak. The results suggest that the coordinated acetate basically dissociates from the POM skeleton when 2 was dissolved in water. Furthermore, the dissociation of acetate was confirmed by ESI-MS. A series of negatively 4-charged polyanion species are found in Figure 4, where the highest peak centered at m/z = 642.30 can be assigned to the protonated POM cluster species ${\rm [HSc_2PW_{10}O_{38}]^{4-}}$, and the neighboring peak centered at m/z = 652.80 can be attributed to the 2-related species, ${NaSc_2(H_2O)PW_{10}O_{38}}^{4-}$. The other peaks and assignments



Figure 3. ¹³C NMR spectra of compound 2 before and after adding equivalent NaAc.

are summarized in Table S4. The ESI-MS analysis reflects two important points: (i) the Keggin skeleton of 2 is stable in aqueous solution, which is consistent with the results of ^{31}P NMR and IR; (ii) the two CH₃COO⁻ ligands of Sc center can be removed easily and replaced by other ligands.

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Due to the dissociation of acetate ligand in solution, two coordinatively unsaturated Sc centers are formed in **2** and the open Lewis acid sites can facilitate their binding with DMNP, thereby accelerating the hydrolysis rate. Although the Sc center in **1** is also coordinatively unsaturated and can coordinate with DMNP, owing to the existence of aqua ligand, it is less active than the Sc centers in **2**. To further investigate the mechanism of DMNP catalyzed by **2**, Na₂HPO₄ (0.02 mmol) as a competitive ligand was added in the hydrolysis reaction. At the beginning, the reaction solution was clear and then became turbid after 1 h, forming white precipitate. Therefore, we compared the conversion of DMNP in 30 min with and without Na₂HPO₄. As shown in Figure S17, only 2% of DMNP is converted in 30 min in the presence of Na₂HPO₄, which is obviously lower than the conversion (11%) in the absence of Na_2HPO_4 . It is likely that Na_2HPO_4 competes with DMNP for binding with the Sc center, consequently decreasing the reactivity of **2**. A similar rate-decelerating effect of Na_2HPO_4 has also been found in the hydrolysis of DMNP catalyzed by Zr-containing POM.²³

On the basis of above experimental data and previous hydrolysis investigations in the Zr-POM system, we propose a possible mechanism for the DMNP hydrolysis catalyzed by di-Sc-substituted POM (Scheme 3). First, the dissociation of acetate in 2 results in two coordinatively unsaturated Sc centers. Subsequently, the exposed Lewis acid sites coordinate with the phosphoryl oxygen (P = O) of DMNP to form **b**, followed by the addition of water molecules. The hydrolysis reaction is initiated by the nucleophilic attack of agua ligand to DMNP giving a pentacoordinated P intermediate d. After proton transfer from H₂O to DMNP, the elimination of pnitrophenol happens, leaving an intermediate e, where dimethyl ester of phosphoric acid binds the Sc center of POM. The catalytic cycle is completed by the dissociation of dimethyl ester of phosphoric acid. Moreover, the ESI-MS analysis of the reaction solution before and after the catalytic hydrolysis provides us some valuable information. As shown in Figure S18, all peaks found in the spectra are related to the di-Sc-substituted polyanion, confirming the structural integrity of 2 during turnover conditions. More importantly, several intermediate e-related species, e.g., {NaHSc₂(HPO₄C₂H₆)- $PW_{10}O_{38}^{3-}$ (m/z = 906.06), {NaH₂Sc₂(HPO₄C₂H₆)₂-PW₁₀O₃₈²⁻ (m/z = 1421.58), and {NaH₂Sc₂(HPO₄C₂H₆)₂- $PW_{10}O_{38}(H_2O)$ ²⁻ (*m*/*z* = 1431.59), are observed in the ESI-MS spectrum after the catalytic reaction, further supporting the proposed mechanism.

Scheme 3. Proposed Mechanism for the Decontamination of DMNP by Compound 2



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4. CONCLUSIONS

In summary, two novel Sc-substituted Keggin-type POMs, 1 and 2, have been successfully synthesized by controlling the pH value and concentration of HAc/NaAc buffer. The two polyanions not only exhibit good water-solubility and stability in a relatively wide pH range but also can effectively catalyze the hydrolysis of nerve agent simulant, DMNP. The control experiments indicate that the substituted Sc are predominant catalytic active sites, and the impact of Sc coordination environment on their catalytic performance has been studied. This study will shed light on the design and application of Scbased hydrolysis catalysts and promote the understanding of the decontamination mechanism catalyzed by Lewis acidic centers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00976.

Some structural figures, crystal data, selected bond lengths, ESI-MS spectra and assignments, PXRD patterns, IR spectra, ³¹P NMR spectra, UV-vis spectra, and catalytic data (PDF)

Accession Codes

CCDC 1991918–1991919 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

Di Zhang performed the catalytic decontamination of DMNP, and Wenqi Zhang synthesized the two Sc-substituted POMs. Jing Dong and Ni Zhen analyzed part of the data. Structure refinements and ESI-MS analysis were performed by Zhengguo Lin. Prof. Yingnan Chi and Prof. Changwen Hu supervised the project.

Author Contributions

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Notes

The authors declare no competing financial interest.

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