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Gallium(III)-Containing, Sandwich-Type Heteropolytungstates: Synthesis, Solution Characterization, and Hydrolytic Studies toward Phosphoester and Phosphoanhydride Bond Cleavage

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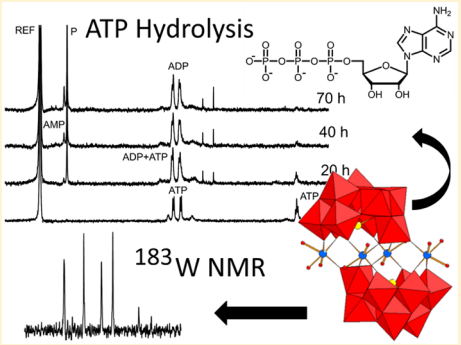
Supporting Information

ABSTRACT: The gallium(III)-containing heteropolytungstates $[Ga_4(H_2O)_{10}(\beta\text{-}XW_9O_{33})_2]^{6-}$ (X = As^{III}, **1**; Sb^{III}, **2**) were synthesized in aqueous acidic medium by reaction of Ga^{3+} ions with the trilacunary, lone-pair-containing $[XW_9O_{33}]^{9-}$. Polyanions **1** and **2** are isostructural and crystallized as the hydrated sodium salts $Na_6[Ga_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33})_2]\cdot 28H_2O$ (**Na-1**) and $Na_6[Ga_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]\cdot 30H_2O$ (**Na-2**) in the monoclinic space group $P2_1/c$, with unit cell parameters a = 16.0218(12) Å, b = 15.2044(10) Å, c = 20.0821(12) Å, and β = 95.82(0)°, as well as a = 16.0912(5) Å, b = 15.2178(5) Å, c = 20.1047(5) Å, and β = 96.2(0)°, respectively. The corresponding tellurium(IV) derivative $[Ga_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]^{4-}$ (**3**) was also prepared, by direct reaction of sodium tungstate, tellurium(IV) oxide, and gallium nitrate. Polyanion **3** crystallized as the mixed rubidium/sodium salt $Rb_2Na_2[Ga_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]\cdot 28H_2O$ (**RbNa-3**) in the triclinic space group $P\bar{1}$ with unit cell parameters a = 12.5629(15) Å, b = 13.2208(18) Å, c = 15.474(2) Å, α = 80.52(1)°, β = 84.37(1)°, and γ = 65.83(1)°. All polyanions **1**−**3** were characterized in the solid state by single-crystal XRD, FT-IR, TGA, and elemental analysis, and polyanion **2** was also characterized in solution by ^{183}W NMR and UV−vis spectroscopy. Polyanion **2** was used as a homogeneous catalyst toward adenosine triphosphate (ATP) and the DNA model substrate 4-nitrophenylphosphate, monitored by ^{1}H and ^{31}P NMR spectroscopy. The encapsulated gallium(III) centers in **2** promote the Lewis acidic synergistic activation of the hydrolysis of ATP and DNA model substrates at a higher rate in near-physiological conditions. A strong interaction of **2** with the P−O bond of ATP was evidenced by changes in chemical shift values and line broadening of the ^{31}P nucleus in ATP upon addition of the polyanion.



INTRODUCTION

Polyoxometalates (POMs) are a large subclass of inorganic compounds, which can frequently be prepared by self-assembly of oxo-anions of early transition metals in high oxidation states (Mo^{VI}, W^{VI}, V^V) in aqueous, acidic medium.[1] The chemical and physical properties of POMs such as shape, size, composition, charge, acidity, redox behavior, and solubility can be easily modified.[2] The structural and compositional versatility of these nanosized, molecular inorganic anions translates to amazing notable applications in various research domains, such as homogeneous and heterogeneous catalysis, materials science, and medicine.[3]

Keggin-type polyanions such as $[PW_{12}O_{40}]^{3-}$ are of special interest for POM researchers, due to their ability to form several lacunary (vacant) derivatives by loss of one or more WO_6 addenda units, such as $[PW_{11}O_{39}]^{7-}$ or $[PW_9O_{34}]^{9-}$.[1a] These species can be considered as inorganic ligands possessing nucleophilic oxygen atoms at the lacunary site, which can coordinate to suitable metal ions.[4] Such work has resulted predominantly in dimeric, sandwich-type structures, namely, the Weakley-type $[M_4(B\text{-}\alpha\text{-}XW_9O_{34})_2]^{n-}$,[5] the Knoth-type $[M_3(A\text{-}\alpha/\beta\text{-}XW_9O_{34})_2]^{n-}$,[6] the Hervé-type $[M_3(B\text{-}\alpha\text{-}XW_9O_{33})_2]^{n-}$,[7] and the Krebs-type $[M_4(B\text{-}\beta\text{-}XW_9O_{33})_2]^{n-}$.[8] Sometimes unexpected structures can be obtained, mainly depending on the reaction conditions.[9]

In 1997, Krebs' group reported a sandwich-type structure series comprising two lone-pair-containing trilacunary 9-tungstoantimonate(III) units, two 3*d* transition metal centers, and two extra tungsten centers, with the general formula $[M_2(H_2O)_6(WO_2)_2(\beta\text{-}SbW_9O_{33})_2]^{(14-2n)-}$ (M^{n+} = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}), by reaction of the transition metal ions with $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$ in aqueous acidic medium.[8a] Further isostructural derivatives such as $[M_2(H_2O)_6(WO_2)_2(\beta\text{-}BiW_9O_{33})_2]^{(14-2n)-}$ (M^{n+} = Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}), $[(VO(H_2O)_2)_2(WO_2)_2(\beta\text{-}BiW_9O_{33})_2]^{10-}$, and $[Sn_{1.5}(WO_2(OH))_{0.5}(WO_2)_2(\beta\text{-}XW_9O_{33})_2]^{10.5-}$ (X = Sb, Bi)[8b,c]

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have also been reported by the same group. The first tetra-substituted structure of the Krebs-type, $[Mn_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]^{8-}$, was reported in 1998.[10] Some additional derivatives with other occupancies in the four guest metal sites are also known, such as $[M_3(H_2O)_8(WO_2)(\beta\text{-}TeW_9O_{33})_2]^{8-}$ (M = Ni^{2+}, Co^{2+}), $[(Zn(H_2O)_3)_2(WO_2)_{1.5}(Zn(H_2O)_2)_{0.5}(\beta\text{-}TeW_9O_{33})_2]^{8-}$, and $[(VO(H_2O)_2)_{1.5}(WO(H_2O)_2)_{0.5}(WO_2)_{0.5}(VO(H_2O))_{1.5}(\beta\text{-}TeW_9O_{33})_2]^{7-}$.[11]

Our group has also worked extensively in this area, and we reported $[Fe_4(H_2O)_{10}(\beta\text{-}XW_9O_{33})_2]^{n-}$ (X = As^{III}, Sb^{III}, n = 6, X = Se^{IV}, n = 4),[12a] $[In_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33}H)_2]^{4-}$, and $[In_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]^{6-}$,[12b] as well as $[Al_4(H_2O)_{10}(\beta\text{-}XW_9O_{33}H)_2]^{4-}$ (X = As^{III}, Sb^{III}),[12c] which were all obtained by reaction of the respective lone-pair-containing trilacunary POM precursor with the corresponding metal ions. More recently, we reported the mono- and di-rare-earth-containing 21- and 20-tungstoantimonates(III) $[Ln(H_2O)_4Sb_2W_{21}O_{72}(OH)]^{10-}$ (Ln = Yb^{3+}, Lu^{3+}) and $[Ln_2(H_2O)_8Sb_2W_{20}O_{70}]^{8-}$ (Ln = Yb^{3+}, Lu^{3+}, Y^{3+}), by reaction of $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$ with Ln^{3+} at different pH.[13] Some other derivatives have also been prepared and their catalytic properties studied, such as water oxidation,[14] epoxidation of alkenes,[12c,15] Mannich-type reactions,[16] and bio-inspired oxygenation.[17]

Phosphoester bonds are characterized by a high stability, as they play an important role in protecting our genetic material.[18] However, in the last decades much attention has been paid to the controlled cleavage of this relatively inert bond as a vital step in several biochemical techniques. Being inspired by nature, most researchers look toward the use of metal ion-containing catalysts as new artificial phosphoesterase. Many reports in the literature can be found on the cleavage of DNA model substrates by structurally different metal ion complexes.[19] The Parac-Vogt group has already extensively explored the biological activity of POMs toward the cleavage of phosphoester bonds in numerous DNA and RNA model substrates.[20] Initially, several isopolyanions were studied for the kinetics and underlying mechanism of the hydrolysis of DNA model substrates. In the case of heptamolybdate $[Mo_7O_{24}]^{6-}$, hydrolysis of the phosphoester bond results from destabilization by incorporation of the substrate into the POM framework.[20a] Decavanadate $[V_{10}O_{28}]^{6-}$ was also found to catalyze the hydrolysis reaction by a fast and reversible dissociation of the POM structure, after which the substrate could bind and be activated by the smaller POM fragments.[20b] In different studies, several metal-ion-substituted heteropolytungstates were screened for phosphoesterase activity against DNA and RNA model substrates.[20f−i] In this approach, the expected activity results from the Lewis-acidic properties of the incorporated metal ion, while the POM acts as a stabilizing ligand, keeping the metal ion in its active form.

Very little work has been carried out on gallium-containing POMs to date, and in the few known compounds gallium is largely present as a tetrahedrally coordinated primary heteroatom, such as in the Keggin-type compounds $H_5GaW_{12}O_{40}$ and $[\alpha\text{-}GaW_9O_{34}H_2]^{9-}$, respectively.[21] The latter was employed to synthesize the trivanadium-substituted derivative $[\alpha\text{-}GaW_9V_3O_{40}]^{8-}$, as based on solution studies (^{51}V and ^{183}W NMR).[22] Solution studies of other isostrucural derivatives were also reported, such as $[\beta\text{-}GaW_9M_3O_{40}]^{n-}$ (M = Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, V^{5+}).[23] In 2005, Krebs' group structurally characterized the Weakley-type dimers $[M_4(H_2O)_2(GaW_9O_{34})_2]^{14-}$ (M = Cu^{2+}, Zn^{2+}) by single-crystal XRD.[24] Interaction of gallium(III) salts such as $Ga(NO_3)_3$ or $GaCl_3$ with monolacunary Keggin-type ions $[\alpha\text{-}XW_{11}O_{39}]^{n-}$ (X = B^{III}, n = 9; Si^{IV}, Ge^{IV}, n = 8; P^{V}, As^{V}, n = 7), trilacunary Keggin-type ions $[\alpha/\beta\text{-}XW_9O_{34}]^{10-}$ (X = Si^{IV}, Ge^{IV}), and monolacunary Wells−Dawson-type ions $[X_2W_{17}O_{61}]^{10-}$ (X = P^{V}, As^{V}) has been studied by several research groups, and the products were investigated by ^{183}W NMR spectroscopy and other analytical techniques (FT-IR, FAB mass spectrometry, electrochemistry, and thermogravimetric analysis).[25] Patzke's group synthesized two gallium(III)-containing tungstosilicates(IV), $[Ga_6(H_2O)_3(\alpha\text{-}SiW_9O_{35}(OH)_2)_2]^{10-}$ and $[Ga_4(H_2O)_2\{\alpha\text{-}SiW_{10}O_{38}\}_2]^{12-}$, and studied their solid-state and solution properties.[26]

Here we report on the synthesis and structural characterization of gallium(III)-containing heteropolyanions of the Krebs-type and their activity as homogeneous catalysts for the hydrolysis of the DNA model substrates 4-nitrophenylphosphate (NPP) and adenosine triphosphate (ATP).

EXPERIMENTAL SECTION

General Procedures. All reagents were used as purchased without further purification. The trilacunary POM precursor salts $Na_9[B\text{-}\alpha\text{-}AsW_9O_{33}]\cdot 19.5H_2O$ and $Na_9[B\text{-}\alpha\text{-}SbW_9O_{33}]\cdot 19.5H_2O$ were synthesized according to the literature, and their purity was confirmed by FT-IR.[8a,27] The infrared (IR) spectra for the solid samples were obtained on KBr pellets using a Nicolet Avatar 370 FTIR spectrophotometer. The solution ^{183}W NMR spectra of the obtained compounds were recorded on a 400 MHz JEOL ECX instrument at room temperature, using 10 mm tubes. The solution ^{1}H and ^{31}P NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at room temperature using 5 mm tubes. The respective resonance frequencies were 399.78 MHz (^{1}H), 161.975 MHz (^{31}P), and 16.69 MHz (^{183}W). The ^{1}H, ^{31}P, and ^{183}W chemical shifts are respectively referenced to TMSPA-d_4, trimethylphosphate, and 1 M Na_2WO_4(aq). Thermogravimetric analyses were carried out on a TA Instruments SDT Q600 instrument, using 10−30 mg of sample in 100 μL alumina pans under a 100 mL/min flow of nitrogen; the temperature was ramped from 20 to 1000 °C at a rate of 5 °C/min. Elemental analyses were performed at Institut des Sciences Analytiques, Villeurbanne, France.

X-ray Crystallography. Single crystals of **Na-1**, **Na-2**, and **RbNa-3** were mounted on a Hampton cryoloop in light oil for data collection at 100 K. Indexing and data collection were measured on a Bruker D8 SMART APEX II CCD diffractometer with kappa geometry (graphite monochromator, $\lambda_{Mo\ K\alpha}$ = 0.710 73 Å. Data integration was performed using SAINT.[28] Routine Lorentz and polarization corrections were applied. Multiscan absorption corrections were performed using SADABS. Direct methods (SHELXS) successfully located the tungsten atoms, and successive Fourier syntheses (SHELXL) revealed the remaining atoms.[29] Refinements were full matrix least-squares against $|F|^2$ using all data. In the final refinement, the Ga, As, Sb, Te, W, Na, and Rb atoms were refined anisotropically, whereas the O atoms and disordered countercations were refined isotropically.

Synthesis of $Na_6[Ga_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33})_2]\cdot 28H_2O$ (Na-1). $GaCl_3$ (1.080 mL of a 0.514 M aqueous solution, 0.555 mmol) was directly added to $Na_9[B\text{-}\alpha\text{-}AsW_9O_{33}]\cdot 19.5H_2O$ (0.737 g, 0.250 mmol) in 20 mL of water. The pH of the resulting colorless solution was adjusted to 3 by using 2 M HCl. The solution was then heated to 80 °C for 1 h, then allowed to cool to room temperature. Colorless crystals were formed after 2 to 3 weeks with a yield of 0.47 g (33%). IR: 3408(vs), 965(vs), 908(w), 826(s), 689(s), 472(m), 430(w) Anal. Calcd (found): As 2.67 (2.75), Ga 4.96 (4.97), Na 2.45 (2.36), W 58.91 (58.51).

Synthesis of $Na_6[Ga_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]\cdot 30H_2O$ (Na-2). $GaCl_3$ (1.080 mL of a 0.514 M aqueous solution, 0.555 mmol) was directly added to $Na_9[B\text{-}\alpha\text{-}SbW_9O_{33}]\cdot 19.5\ H_2O$ (0.715 g, 0.25 mmol) in 20 mL of water. The pH of the resulting colorless solution was adjusted to 3 by using 2 M HCl. The solution was then heated to 80 °C for 1 h, then allowed to cool to room temperature. The color of the reaction mixture then changed to pale yellow, and colorless crystals were formed after 2 to 3 days with a yield of 0.72 g (51%). IR: 3420(vs),

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958(s), 897(w), 814(s), 668(s), 470(m), 420(vw) Anal. Calc (found): Sb 4.24 (4.32), Ga 4.85 (4.69), Na 2.40 (2.35), W 57.59 (56.79).

Synthesis of $Rb_2Na_2[Ga_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]\cdot 28H_2O$ (RbNa-3). TeO_2 (61.28 mg, 0.384 mmol) was dissolved in a minimum amount of concentrated HCl and added directly to $Na_2WO_4\cdot 2H_2O$ (1.140 g, 3.456 mmol) in 10 mL of water. The pH of the solution was adjusted to 5.8 by using 4 M NaOH, and the reaction mixture was heated to 70 °C for 10 min, and then allowed to cool to room temperature. $Ga(NO_3)_3$ (0.197 g, 0.768 mmol) was directly added and the solution was further stirred at room temperature for 1 h. Addition of 0.5 mL of 0.5 M RbCl and slow evaporation at room temperature resulted in colorless single crystals after 2 to 3 weeks, with a yield of 0.83 g (37%). IR: 3418(vs), 974(vs), 880(vw), 819(vs), 746(m), 700(s), 662(m), 489(m). Anal. Calcd (found): Te 4.55 (4.42), Ga 4.81 (4.62), Rb 2.95 (2.97), Na 0.80 (0.93), W 57.04 (56.74).

Polyanions **1**−**3** could also be synthesized using $Ga(NO_3)_3$ instead of $GaCl_3$.

Hydrolysis Experiments. Hydrolysis experiments were performed by mixing compound **Na-2**, dissolved in hot 100 mM LiCl in D_2O, with the substrate. TMSPA-d_4 (trimethylsilylpropionic acid-d_4) as a water-soluble reference was added to samples needing ^1H NMR characterization. After mixing, the pD value of the solutions was adjusted by the addition of DCl or NaOD. The pD value was calculated using the formula pD = pH + 0.41. The reaction mixtures were heated in a heating block or oil bath, and the reactions followed by means of ^1H or ^{31}P NMR spectroscopy after different time intervals. The integration of the peaks corresponding to start and end products was used to calculate the progress and kinetics of the reaction.

RESULTS AND DISCUSSION

The respective interaction between the lone-pair-containing trilacunary POM precursors $[XW_9O_{33}]^{9-}$ (X = As^{III}, Sb^{III}) with Ga^{3+} ions in slightly acidic aqueous medium resulted in the formation of the two polyanions $[Ga_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33})_2]^{6-}$ (**1**) and $[Ga_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]^{6-}$ (**2**), which were isolated in crystalline form as hydrated sodium salts $Na_6[Ga_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33})_2]\cdot 28H_2O$ (**Na-1**) and $Na_6[Ga_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]\cdot 30H_2O$ (**Na-2**), respectively. Both salts crystallize in the monoclinic space group $P2_1/c$ and are isomorphous. For tellurium(IV), the stoichiometric reaction of TeO_2 or TeO_3^{2-} and Na_2WO_4 is known to produce the trilacunary $[TeW_9O_{33}]^{8-}$ unit, as reported by Pope and co-workers.[30] We adapted this approach in order to prepare the tellurium(IV) analogue $[Ga_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]^{4-}$ (**3**), which crystallized as mixed rubidium/sodium salt $Rb_2Na_2[Ga_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]\cdot 28H_2O$ (**RbNa-3**) in the triclinic space group $P\bar{1}$.

Polyanions **1**−**3** are isostructural and of the Krebs-type, which consists of two equivalent $\{\beta\text{-}XW_9O_{33}\}$ units linked by four octahedrally coordinated Ga^{3+} ions, resulting in a structure with idealized C_{2h} symmetry (Figure 1). The four Ga^{3+} ions are arranged in pairs at two positions: an outer position with three terminal aqua ligands and an inner one with two. Krebs and co-workers have previously suggested a formation mechanism of the structure involving insertion, isomerization, and dimerization.[8a] As a matter of fact, both $[\alpha\text{-}SbW_9O_{33}]^{9-}$ and $[\beta\text{-}SbW_9O_{33}]^{9-}$ isomers were identified in aqueous solution by the same group, with the "α" isomer dominating at neutral pH and the "β" one in acidic pH.[8a] The α-based Hervé-type sandwich dimer, which forms in neutral pH, supports this hypothesis, as we have also previously reported.[7,31]

It is worth noting that the charges of polyanions **1** (6−), **2** (6−), and **3** (4−) fall within the range of our previously reported Krebs-type compounds containing trivalent metal cations, namely, $[Fe_4(H_2O)_{10}(\beta\text{-}XW_9O_{33})_2]^{n-}$ (X = As^{III}, Sb^{III}, n = 6, X = Se^{IV}, n = 4), $[In_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33}H)_2]^{4-}$, $[In_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]^{6-}$, and $[Al_4(H_2O)_{10}(\beta\text{-}XW_9O_{33}H)_2]^{4-}$ (X = As^{III}, Sb^{III}),[12] strongly suggesting that tetra-substituted Krebs-type POMs are most stable within this charge range. Contrary to the aluminum(III) and indium(III) analogues, no protonation sites were identified within the POM skeleton of **1**−**3**, as checked by bond valence sum calculations, which showed that all terminal ligands of the gallium atoms are water molecules, and confirmed the expected oxidation states of the heteroatom (As^{III}, Sb^{III}, Te^{IV}), Ga^{III}, and W^{VI} centers.[32]

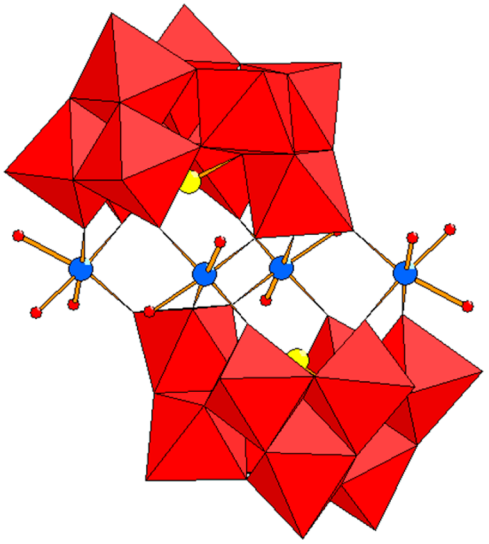

Figure 1. Combined polyhedral/ball-and-stick representation of $[Ga_4(H_2O)_{10}(B\text{-}\beta\text{-}XW_9O_{33})_2]^{n-}$ (X = As, 1; Sb, 2; n = 6, X = Te, 3; n = 4). Color code: WO_6, red octahedra; Ga, blue; As, Sb, Te yellow; O, red.

Polyanions **1**−**3** have similar Ga−O bond lengths, which fall in the range 1.892(7)−1.957(7) Å for **1**, 1.900(7)−1.988(7) Å for **2**, and 1.897(9)−2.025(10) Å for **3**, respectively. As expected, the average As^{III}−O bond lengths (1.799(6) Å) in **1** are shorter than Te^{IV}−O (1.893(9) Å) in **2** and Sb^{III}−O (1.999(7) Å) in **3**. On the other hand, the corresponding heteroatom distances As···As (ca. 5.98 Å) and Sb···Sb (ca. 5.61 Å) are between those of our reported $[Al_4(H_2O)_{10}(\beta\text{-}XW_9O_{33}H)_2]^{4-}$ (X = As, Sb) (As···As = 5.92 Å, Sb···Sb = 5.87 Å), $[In_4(H_2O)_{10}(\beta\text{-}AsW_9O_{33}H)_2]^{4-}$ (As···As = 6.26 Å), and $[In_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]^{6-}$ (Sb···Sb= 5.87 Å), reflecting the size differences of the incorporated guest ions Ga^{III}, Al^{III}, and In^{III}, respectively. Selected bond lengths and angles of polyanions **1**−**3** are shown in Table 1, and crystal data are shown in Table S1 (Supporting Information).

The solid-state FT-IR spectra (Figure S1) of compounds **Na-1**, **Na-2**, and **RbNa-3** show very similar absorbance peaks in the polyanion metal-oxo region. All three compounds showed bands around 960(s), 895(w), and 820(s), corresponding to W−O terminal as well as corner- and edge-shared WO_6 stretching frequencies, respectively. The thermal stability of the three salts **Na-1**, **Na-2**, and **RbNa-3** was also investigated by thermogravimetric analysis (TGA). All three compounds show one main weight loss step until ca. 400 °C, which is attributed to the loss of crystal and coordinated water molecules. No significant weight loss was observed above 400 °C, and the compounds decomposed eventually to their respective metal oxides at higher temperatures (Figure S2).

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Table 1. Selected Bond Lengths and Angles for Polyanions 1−3

1	2	3
As−O 1.799(6)	Sb−O 1.999(7)	Te−O 1.893(9)
As−As 5.977(14)	Sb−Sb 5.607(9)	Te−Te 5.702(13)
Ga1−O3A 1.900(7)	Ga1−O2A 1.903(7)	Ga1−O5A 1.921(8)
Ga1−O4A 1.892(7)	Ga1−O6A 1.900(7)	Ga1−O9A 1.894(8)
Ga1−O8A 1.946(7)	Ga1−O7A 1.988(7)	Ga1−O2A 1.928(8)
Ga1−O8B 1.924(7)	Ga1−O7B 1.970(7)	Ga1−O2B 1.950(8)
Ga1−O1G1 2.055(7)	Ga1−O1G1 2.024 (7)	Ga1−O1G1 1.995(9)
Ga1−O2G1 2.068(7)	Ga1−O2G1 2.015(7)	Ga1−O2G1 2.033(9)
Ga2−O7A 1.924(7)	Ga2−O3A 1.933(7)	Ga2−O4A 1.938(10)
Ga2−O9A 1.934(7)	Ga2−O7T 1.955(7)	Ga2−O2T 2.034(8)
Ga2−O8T 1.957(7)	Ga2−O4G2 1.928(7)	Ga2−O4G2 1.985(8)
Ga2−O1G2 1.977(7)	Ga2−O1G2 1.975(7)	Ga2−O1G2 1.926(13)
Ga2−O2G2 1.950(7)	Ga2−O2G2 1.947(8)	Ga2−O2G2 1.947(11)
Ga2−O3G2 2.092(7)	Ga2−O3G2 2.101(7)	Ga2−O3G2 1.962(9)
Ga1−O3A−W3 144.3(4)	Ga1−O2A−W2 141.6(4)	Ga1−O5A−W5 142.6(5)
Ga1−O4A−W4 143.2(4)	Ga1−O6A−W6 143.5(4)	Ga1−O9A−W9 140.9(5)
Ga1−O8A−W8 173.7(4)	Ga1−O7A−W7 175.7(4)	Ga1−O2A−W2 172.2(5)
Ga1−O8B−W8 175.5(4)	Ga1−O7B−W7 177.6(4)	Ga1−O2B−W2 177.7(5)
Ga2−O7A−W7 136.9(4)	Ga2−O3A−W3 136.9(4)	Ga2−O4A−W4 133.4(5)
Ga2−O9A−W9 134.3(4)	Ga2−O4G2−W5 134.9(4)	Ga2−O4G2−W7 134.1(5)
Ga2−O8T−W8 165.2(4)	Ga2−O7T−W7 165.9(4)	Ga2−O2T−W2 168.7(6)

The solution behavior of all three polyanions **1**−**3** was also studied by ^{183}W NMR. The ^{183}W NMR spectrum of a freshly prepared solution of **Na-2** in 0.1 M HCl showed five signals at −118, −132, −144, −152, and −170 ppm, respectively, with relative intensities 2:2:2:2:1 (Figure 2), which is fully consistent

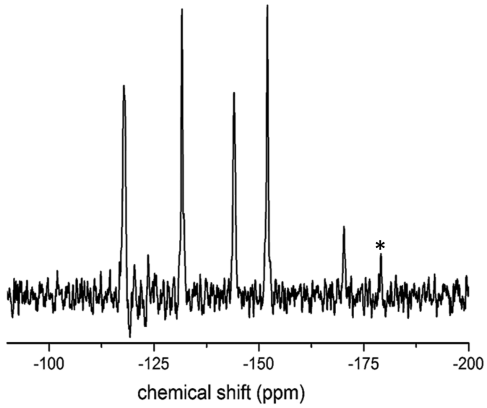

Figure 2. ^{183}W spectrum of polyanion **2** in 0.1 M HCl (* possible impurity signal).

with the C_{2h} symmetry of polyanion **2** in the solid state. The arsenic analogue **Na-1** showed insufficient stability in 0.1 M HCl during the measurement time, as based on multiple peaks in the spectrum that could not be assigned, whereas the solubility of **RbNa-3** in water was too low, even after countercation exchange.

Additionally, the UV−vis spectrum of **Na-2** displays an absorption at 256 nm, which is mainly attributed to charge transfer of the W═O bonds in **2**. Time-dependent UV−vis spectra of **Na-2** were also measured, and no significant change was observed after 24 h. As based on the above solution studies, we concluded that polyanion **2** is stable enough for performing meaningful hydrolytic studies of phosphoester bonds.

Hydrolysis of Phosphoester Bond. Over the last two decades, several studies were performed to explore the hydrolysis of phosphoester bonds by metal ion complexes. Typically, the metal ions possess at least two available coordination sites in order to display any phosphoesterase activity, where one allows the coordination of the substrate while the other one serves to deliver a coordinated water molecule, which serves as a nucleophile in the hydrolysis reaction.[33] The crystal structure of polyanion **2** showed that the inner gallium(III) ions have two water molecules and the outer gallium(III) atoms contain three water molecules attached. It is very apparent that **2** has many available coordination sites, which can be easily substituted by the substrate. Together with several possible cooperative gallium(III) ions, this compound seems ideally suited for hydrolysis of phosphoester bonds and might enhance the rate of the hydrolysis. In our study, we focused our attention on compound **2** toward the hydrolysis of phosphoester bonds. For this purpose we used 4-nitrophenylphosphate, which is commonly used as a substrate in enzymatic studies,[34] as well as a model substrate in studies focusing on the development of artificial metallonucleases.[35] NPP is very resistant to hydrolysis, with a half-life of 135 days at pH 5.0 and 50 °C in the absence of a catalyst.[20d]

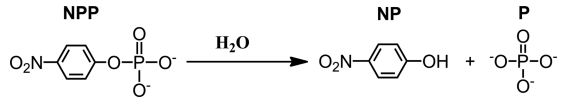

Figure 3. General model of hydrolysis of 4-nitrophenylphosphate (NPP).

To explore the hydrolytic activity of polyanion **2**, the hydrolysis reaction with NPP was carried out and monitored by ^{1}H NMR spectroscopy. In addition, the hydrolysis of ATP was followed by ^{31}P NMR spectroscopy. The solubility of **2** is poor in water, so we performed all reactions in the presence of LiCl in D_2O in order to increase its solubility. In a typical experiment, a reaction mixture was prepared containing 0.5 mM polyanion **2** and 1 mM NPP (1:2 ratio) in 100 mM LiCl in D_2O, and then heated to 60 °C. The reaction mixture was kept at this temperature, and ^{1}H NMR spectra were taken at certain time intervals. More detailed ^{1}H NMR (Figure 4) spectra showed that

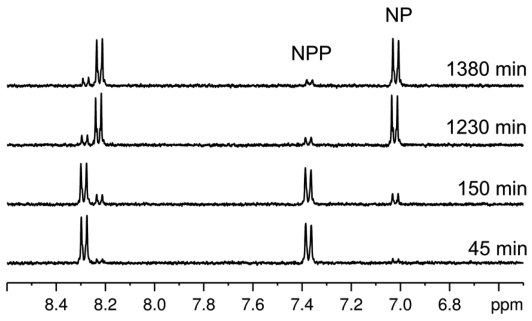

Figure 4. ^{1}H NMR spectra of the hydrolysis of 1 mM NPP with 0.5 mM **2** at pD 5 and 60 °C.

complete hydrolysis of NPP occurred within 24 h. During the reaction a gradual disappearance of the doublets assigned to NPP can be seen, while two new doublets appear, which can be assigned to the newly formed hydrolysis product *p*-nitrophenol (NP). The upfield shift of the NP resonances can be explained by the presence of a hydroxyl group, instead of the phosphate group in NPP.

On the basis of the ^{1}H NMR integration values, the percentage of NPP at different time intervals was calculated and

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the natural logarithm of the concentration of starting product as a function of time was fitted to a first-order decay function to obtain the observed rate constant (Figure S3). However, the kinetic experiments in which the dependence of the reaction rate on catalyst concentration is studied could not be reliably performed due to the very low solubility of the polyanion salt. The hydrolysis reaction in the absence of polyanion **2** was also performed in order to correct for the self-hydrolysis of NPP. The NPP hydrolysis reaction in the presence of **2** was carried out at different pD values, and the rate constants are summarized in Table 2.

Table 2. Rate Constants for the Spontaneous Hydrolysis (k_{uncat}) of 1 mM NPP and in the Presence of 0.5 mM 2 at 60 °C (k_{obsd}) at Various pD Values

pD	k_{obsd}	k_{uncat}	k_{corr} $(min^{-1})^a$
4	1.38×10^{-3}	1.33×10^{-3}	5.00×10^{-5}
5	1.36×10^{-3}	6.93×10^{-4}	6.67×10^{-4}
6	1.26×10^{-3}	1.81×10^{-4}	1.08×10^{-3}
7	3.59×10^{-4}	7.83×10^{-5}	2.81×10^{-4}
8	5.28×10^{-5}	4.95×10^{-5}	3.30×10^{-6}

$^a k_{corr}$ was obtained by subtracting the k_{uncat} value from k_{obsd}.

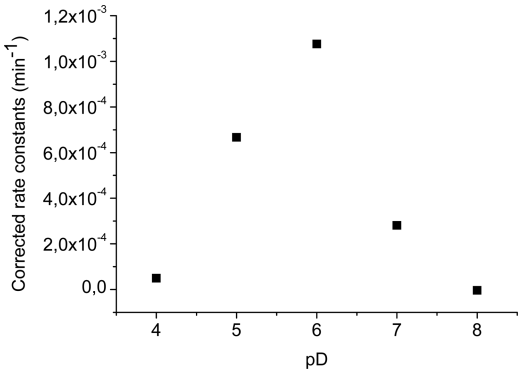

Figure 5. pD dependence of the hydrolysis rate of 1 mM NPP in the presence of 0.5 mM **2** at 60 °C.

Figure 5 shows a bell-shaped pH reactivity profile, which is often observed in phosphate cleavage reactions promoted by metal complexes[36] and indicates that deprotonation of the two acidic metal-bound species results in opposite effects. The first deprotonation leads to a reactivity increase and is commonly associated with the formation of an active nucleophile (i.e., a metal-bound hydroxide), whereas the second deprotonation results in an anionic species that forms an inactive complex with the polyanion.[36]

Interestingly, the isostructural Al derivative $[(Al_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]^{6-}$[12c] shows a comparable reactivity toward NPP. At pD 6 and 7 rate constants of 7.33×10^{-4} min^{-1} and 4.14×10^{-4} min^{-1}, respectively, were observed, which is similar to the rate constants obtained for polyanion **2**. This is not too surprising, considering the identical structure and charge of the two polyanions and comparable Lewis acidity of Ga^{III} and Al^{III}. A comparison of the catalytic activity of **2** with that of the zirconium-containing 32-tungsto-4-phosphate $[Zr_4(P_2W_{16}O_{59})_2(\mu_3\text{-}O)_2(OH)_2(H_2O)_4]^{14-}$ (Zr_4–WD_2), which also contains four strong Lewis acidic metal ions (Zr^{IV}) and shows hydrolytic activity toward NPP,[37] revealed that both polyanions exhibit comparable activity. At pD 6.4 and 50 °C the observed rate constant of 5.06×10^{-3} min^{-1} was calculated for Zr_4–WD_2, which is slightly larger than that found for **2** in this study (1.08×10^{-3} min^{-1} at pD 6). This might be due to the higher coordination number and stronger Lewis acidity of Zr^{IV}, which would result in a better activation of the substrate.

In order to investigate the true need for a POM as ligand for the Lewis-acidic metal ions, the reactions were also performed in the presence of the simple $GaCl_3$ salt. However, even in very small concentrations of $GaCl_3$, precipitates formed in the solution, resulting in the disappearance of ^1H NMR peaks in the spectrum (Figure 6). The exact composition of the precipitate that forms upon addition of $GaCl_3$ is unclear, but based on ^1H NMR it is likely that a complex between Ga^{III} and NPP is formed. The complete disappearance of the aromatic signals of NPP suggests an interaction of the phosphate group with the Ga^{III} ion. On the other hand, no precipitates or gel-type materials were formed in the NMR tubes when we used polyanion **2** for hydrolysis, suggesting that the four Ga^{III} ions in **2** are strongly coordinated to the trilacunary Keggin units and not released in the solution during the catalytic reaction. Nevertheless, it was difficult to proof the solution stability of **2** unequivocally. Due to the low solubility of **Na-2** combined with the low sensitivity of the ^{183}W nucleus (14.3% natural abundance), the ^{183}W NMR measurements at conditions pertinent to the catalytic reactions were not very informative. The ^{71}Ga NMR spectrum of the reaction mixture was also recorded, but the low sensitivity (0.05 relative to ^1H) and quadrupolar nature of the ^{71}Ga nucleus (spin 3/2) resulted in very broad peaks, which could not be conclusively analyzed. In addition, we measured UV–vis spectra of **2** in the presence of NPP, but the UV bands of the POM at 256 nm overlap with the strong UV band of the NPP substrate, which absorbs in the same range, and hence the UV–vis technique was also not very informative. Indirect evidence for the solution stability of **2** was obtained by precipitation of the catalyst after the reaction by addition of tetrabutylammonium bromide (TBABr) and subsequently taking the IR spectrum of the obtained TBA salt of **2** (Figure S4).

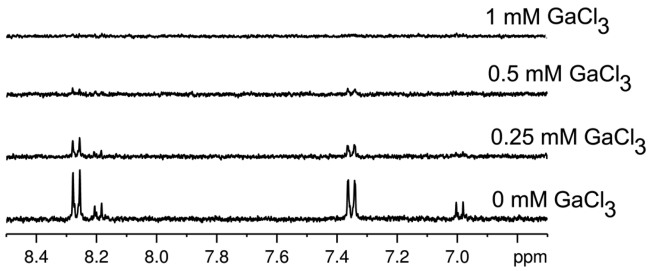

Figure 6. ^1H NMR spectra of 1 mM NPP in the presence of different concentrations of $GaCl_3$.

Hydrolysis of ATP. Adenosine triphosphate, known as a molecular unit of currency of intracellular energy transfer, consists of a sugar molecule with three linked phosphate groups and was used as a substrate in hydrolytic studies screened by ^{31}P NMR spectroscopy. ATP possesses two phosphoanhydride bonds in its molecular structure, and two steps are required for complete hydrolysis. Different concentrations of POM as well as ATP were used in order to understand the solution dynamics of ATP hydrolysis. ^{31}P NMR spectra were taken at different time intervals during the hydrolysis of ATP, in the presence and absence of polyanion **2**.

As can be seen in Figure 7a, there is one triplet at −21.92 ppm and two doublets at −9.73 and −10.45 ppm; these peaks were unambiguously assigned to the central phosphorus (P_β),

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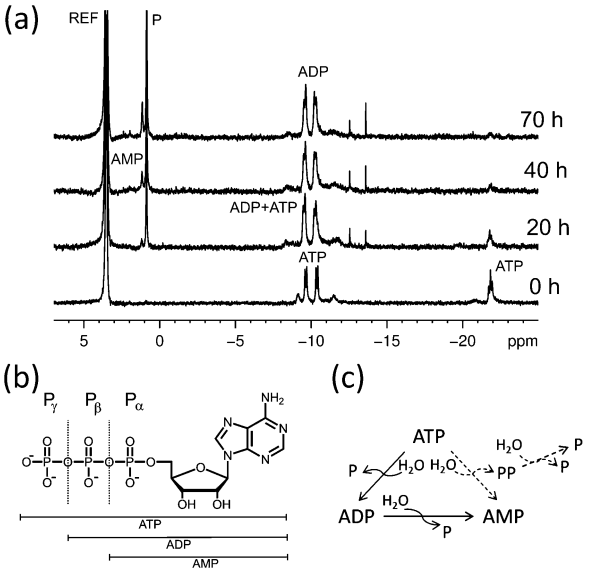

Figure 7. (a) ^{31}P NMR of ATP hydrolysis (20 mM) using 2 mM polyanion **2** in LiCl/H_2O. (b) Adenosine triphosphate structure. (c) Possible stepwise hydrolysis of ATP in the presence of **2**.

terminal phosphorus ($\mathbf{P}_\gamma$), and inner phosphorus ($\mathbf{P}_\alpha$) respectively. In the first stage of hydrolysis reaction, we noticed that first ATP is converted to adenosine diphosphate (ADP) due to the appearance of a singlet at 0.86 ppm and the disappearance of a triplet at −21.85 ppm. The former one is attributed to the presence of free phosphate, while the latter one is due to the disappearance of the signal for the central phosphorus ($\mathbf{P}_\beta$) in ATP, respectively. After almost all the ATP has been converted to ADP, a new singlet around 1.15 ppm starts to appear in the ^{31}P NMR spectrum, which can be attributed to adenosine monophosphate (AMP). This is the result of the hydrolysis of the remaining phosphoanhydride bond in ADP, which releases AMP and another free phosphate. As it is well known that ATP itself undergoes self-hydrolysis in solution, a reaction mixture lacking **2** was monitored at different time intervals to investigate the catalytic power of the polyanion. Only 8% of ATP was converted to ADP in the absence of **2** in the first 20 h, whereas 75% ATP hydrolysis occurred in the presence of the polyanion. The ATP−ADP conversion magnitude slightly increased when the time increased. In total, 19% ATP−ADP self-hydrolysis occurred in the first 40 h, while the hydrolysis yield reached up to 93% in the presence of **2**. This clearly indicates that polyanion **2** acts as an effective homogeneous catalyst toward the hydrolysis of the phosphoanhydride bonds in the ATP structure. From the data obtained, a general model of hydrolysis of ATP is proposed (Figure 7c).

In order to find out the origin for the selectivity of the phosphoanhydride bond hydrolysis in ATP, distinct reaction mixtures were prepared containing different concentrations of polyanion **2** (Figure 8). When 1 mM **2** was present in the reaction mixture, the $\mathbf{P}_\gamma$ and $\mathbf{P}_\beta$ chemical shift values changed about 0.16 and 0.19 ppm, respectively, in comparison with the spectrum of pure ATP, whereas the $\mathbf{P}_\alpha$ values shifted upfield only by 0.05 ppm. The same effect exactly doubled when the concentration of **2** was increased from 1 mM to 2 mM. With further increases of the concentration of **2**, the chemical shift values of $\mathbf{P}_\gamma$ and $\mathbf{P}_\beta$ were affected more, which points toward a fast equilibrium on the NMR time scale for the complexation between POM and ATP. From this experiment it can be

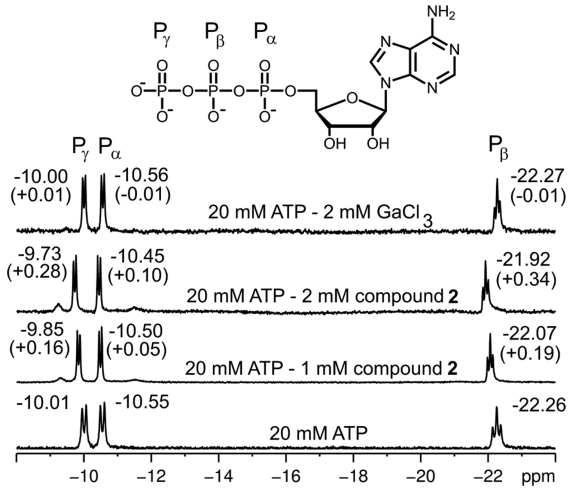

Figure 8. ^{31}P NMR spectra of reaction mixtures containing different concentrations of ATP, polyanion **2**, and $GaCl_3$. The values in brackets represent the chemical shift changes compared to a sample containing 20 mM ATP in the absence of **2**.

concluded that **2** shows a very strong affinity only for $\mathbf{P}_\gamma$ and $\mathbf{P}_\beta$, and the Ga^{III} ions in **2** are selectively coordinated to these, resulting in the activation and hence hydrolysis of the terminal phosphoanhydride bond between $\mathbf{P}_\beta$ and $\mathbf{P}_\gamma$. The same reaction was carried out with free Ga^{III} ions instead of polyanion **2**; surprisingly, no chemical shift changes were observed, which is probably due to the lack of selectivity of free Ga^{III} ions toward the substrate. In this study, we propose that two gallium(III) centers from the same polyanion are involved in the catalysis, and probably one Ga^{III} ion in polyanion **2** is coordinated to the terminal oxygen of the $\mathbf{P}_\gamma$, while a nearby Ga^{III} ion in the structure coordinates to the oxygen atom of $\mathbf{P}_\beta$, thereby activating the phosphoanhydride bond between these two phosphorus atoms. This hypothesis needs to be further supported by theoretical molecular modeling calculations, but the available experimental data indicate that polyanion **2** has some specific, selective properties and performs well as an effective catalyst for the hydrolysis of phosphoanhydride bonds. Very small and broader peaks also appeared during the hydrolysis, which is probably due to a different and stronger complex between the POM and ATP.

CONCLUSIONS

In conclusion, we have successfully synthesized the three gallium-containing, sandwich-type heteropolytungstates $[Ga_4(H_2O)_{10}(\beta\text{-}XW_9O_{33})_2]^{n-}$ (X = As, **1**; Sb, **2**; n = 6; Te, **3**; n = 4) in aqueous acidic medium. Polyanions **1**−**3** have been characterized in the solid state by FT-IR spectroscopy, elemental analysis, TGA, and single-crystal XRD. The solution properties of **2** were studied by ^{183}W NMR and UV−vis spectroscopy, and its catalytic activity toward the hydrolysis of the DNA model substrate NPP and ATP at near physiological pH was followed by ^{31}P NMR. Similar biological studies of other related POM derivatives as well as DFT studies are in progress, and the results will be reported elsewhere.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b01030.

X-ray crystallographic data (CIF)

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X-ray crystallographic data (CIF)
X-ray crystallographic data (CIF)
Solid-state FT-IR and thermograms for **Na-1**, **Na-2**, and **RbNa-3** (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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