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Arylarsonate- and Phosphonate-Capped Polyoxomolybdates, $[(RC_6H_4As)_2Mo_6O_{24}]^{n-}$ and $[(R'C_6H_4P)_2Mo_5O_{21}]^{n-}$

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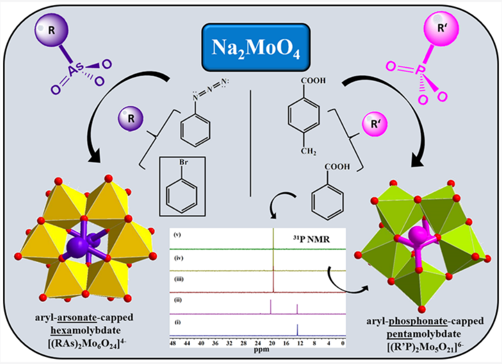

ABSTRACT: We report on the synthesis and structural characterization of four arylarsonate- and phosphonate-capped polyoxomolybdates that exhibit different organic substituents in the para position of the phenyl group. The reaction of arylarsonates ($RAsO_3$, wherein R = 4-BrC_6H_4 or 4-$N_3C_6H_4$) with molybdate in aqueous pH 3.5 media resulted in the cyclic hexamolybdates $[(BrC_6H_4As)_2Mo_6O_{24}]^{4-}$ ($\mathbf{Mo_6As_2L_a}$) and $[(N_3C_6H_4As)_2Mo_6O_{24}]^{4-}$ ($\mathbf{Mo_6As_2L_b}$), whereas the reaction of arylphosphonates ($R'PO_3$, wherein R′ = 4-$O_2CC_6H_4$ or 4-$O_2CC_6H_4CH_2$) with molybdate in aqueous pH 3 media resulted in the cyclic pentamolybdates $[(O_2CC_6H_4P)_2Mo_5O_{21}]^{6-}$ ($\mathbf{Mo_5P_2L_c}$) and $[(HO_2CC_6H_4CH_2P)_2Mo_5O_{21}]^{4-}$ ($\mathbf{Mo_5P_2L_d}$), respectively. Polyanions $\mathbf{Mo_6As_2L_a}$ and $\mathbf{Mo_6As_2L_b}$ comprise a ring of six MoO_6 octahedra that is capped on either side by an organoarsonate group, whereas $\mathbf{Mo_5P_2L_c}$ and $\mathbf{Mo_5P_2L_d}$ consist of a ring of five MoO_6 octahedra that is capped on either side by an organophosphonate group, with the organic arms protruding away from the metal−oxo core of the polyanions. All four polyanions $\mathbf{Mo_6As_2L_a}$, $\mathbf{Mo_6As_2L_b}$, $\mathbf{Mo_5P_2L_c}$, and $\mathbf{Mo_5P_2L_d}$ have been characterized in the solid state by single-crystal X-ray diffraction, IR spectroscopy, and thermogravimetric and elemental analysis and in solution by multinuclear NMR (^{31}P, ^{13}C, and ^1H). The synthetic procedure of (4-bromophenyl)arsonic acid, $BrC_6H_4AsO_3H_2$, is reported here for the first time.

■ INTRODUCTION

Polyoxometalates (POMs) are a rapidly growing class of inorganic compounds because of the multitude of structures and compositions along with impressive redox, photochemical, optical, electronic, magnetic, thermal, and biological properties,[1] rendering POMs important for a wide variety of applications, in particular catalysis but also materials science, biomedicine, electrochromism, sensor technology, and renewable energy.[2] Polyoxotungstates, -molybdates, and -vanadates are usually prepared via condensation reactions in aqueous acidic media. The potential of POMs for pharmaceutical applications due to their anticancer, antitumor, and antiviral activity is well established, but frequently the selectivity toward a specific target remains challenging.[3] In this regard, the covalent grafting of organic groups on the surface of POMs is an elegant and promising strategy.[4] This approach has several advantages, such as precise structural control via the attachment of functional groups (allowing one to fine-tune steric hindrance and polarity), an increase in the stability of POMs at physiological pH, and the possibility of binding to proteins, tissues, and receptors. As the number of POMs with the above features is rather small, it is of major interest to rationally design and synthesize organically functionalized derivatives of POMs that are water-soluble and stable.[5]

Several strategies have been tested by researchers in this regard over the years, such as the grafting amino acids,[4b−e] phosphonates,[6] phosphites,[7] and arsonates[8] onto the surface of POMs. In particular, the organic modification of polyoxovanadates has been explored extensively, utilizing amino acids and carboxylate-containing organic groups.[4d−f,9] Various organophosphonate and -arsonate-stabilized polyoxomolybdates have also been reported, such as the pentamolybdate family $[X_2Mo_5O_{23}]^{n-}$. In 1975, Pope et al. reported the polyanion family $[(RP)_2Mo_5O_{21}]^{4-}$ (R = H, CH_3, C_2H_5, C_6H_5, $C_2H_4NH_3^+$, p-$CH_2C_6H_4NH_3^+$), which are stable in aqueous solution at pH 2.5−5.[4g] In 1988, Sasaki et al. reported the crystal structure of the phosphite derivative $[(HP)_2Mo_5O_{21}]^{4-}$,[7b] and in the same year, the crystal structure of $[(C_6H_5P)_2Mo_5O_{21}]^{4-}$ was reported by Lyxell and Strandberg.[7c] In 2003, our group reported the first examples of phosphonocarboxylate-functionalized polyoxo-5-molybdates, $[(O_2C(CH_2)_nPO_3)_2Mo_5O_{21}]^{6-}$ (n = 1, 2), respectively.[10]

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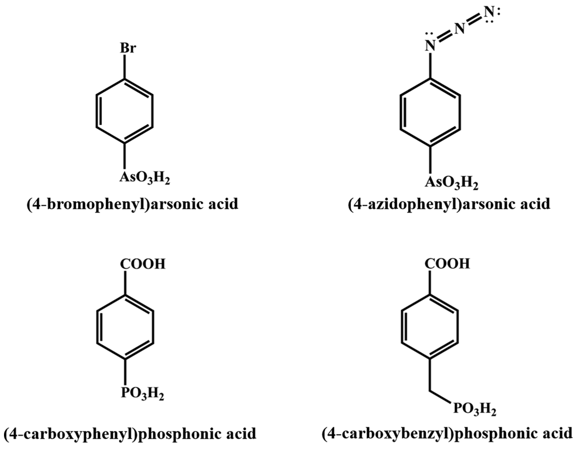
In 1976, Stalick and Quicksall reported the structures of $[(CH_3P)_2Mo_5O_{21}]^{4-}$ and $[(NH_3C_2H_4P)_2Mo_5O_{21}]^{2-}$,[7d] and in the same year, Pope et al. reported several organoarsonate-functionalized polyoxo-6-molybdates, $[(RAs)_2Mo_6O_{24}]^{4-}$ (R = CH_3, Ph, 4-$NH_2C_6H_4$).[11] In 1988, Liu et al. reported the organoarsonate-containing 5-molybdate $[(n\text{-}C_3H_7As)_2Mo_5O_{21}]^{4-}$, and from the same reaction solution, they also isolated the 6-molybdate $[(n\text{-}C_3H_7As)_2Mo_6O_{24}]^{4-}$.[12] Now we decided to expand the family of organophosphonate and -arsonate-containing penta- and hexamolybdates by utilizing para-functionalized phenylphosphonates and -arsonates. Substitution of the phenyl ring in the para position with biologically active groups such as azide ($-N_3$) or carboxylate ($-COOH$) would allow for the resulting polyanion to interact post-synthetically with biological receptors. The azide functional group is suitable for click reactions and the carboxylate group can bind to amino groups, allowing for covalent coupling with peptides, nucleotides, antibodies, etc. Therefore, we were motivated to incorporate the appropriate para-functionalized arylarsonate and -phosphonate groups into the novel polyanions. Here we also report for the first time on the synthesis of (4-bromophenyl)arsonic acid (see the Experimental Section for details).

■ EXPERIMENTAL SECTION

Materials and Physical Measurements. All chemicals were received as reagent-grade from commercial sources and used without further purification. The hetero groups (4-azidophenyl)arsonic acid,[3a] (4-carboxyphenyl)phosphonic acid,[13] and "(4-carboxybenzyl)-phosphonic acid[14] were synthesized following literature procedures (structures shown in Scheme 1). We have developed a synthetic procedure for (4-bromophenyl)arsonic acid (Scheme 1). The NMR spectra (^1H, ^{13}C, and ^{31}P) were recorded at room temperature on a JEOL ECX 400 MHz instrument at Jacobs University. The chemical shifts are reported with respect to the references $Si(CH_3)_4$ (^{13}C and ^1H) and 85% H_3PO_4 (^{31}P), respectively. The IR spectra were recorded on KBr disks using a Nicolet-Avatar 370 spectrometer between 400 and 4000 cm^{-1}. Thermogravimetric analyses were carried out using a TA Instruments Q600 device under the flow of N_2 gas with a heating rate of 5 °C min^{-1} in the temperature range of 30−800 °C. Elemental analyses were performed by Crealins, Villeurbanne, France.

Scheme 1. Structures of the Arylarsonates and -Phosphonates Used in This Study



(4-bromophenyl)arsonic acid (4-azidophenyl)arsonic acid

(4-carboxyphenyl)phosphonic acid (4-carboxybenzyl)phosphonic acid

Synthesis. *(4-Bromophenyl)arsonic Acid, $BrC_6H_4AsO_3H_2$.* *p*-Bromoaniline (3.44 g, 20.0 mmol) was dissolved in 25 mL of a 2 M HCl(aq) solution at 0 °C and allowed to stand at 0 °C for 10 min. Then 5 mL of a 0.1 mM aqueous $NaNO_2$ solution was added dropwise, and the mixture was stirred for 15 min at 0 °C (solution 1). In a separate beaker, 25 mL of water was heated to 80 °C and then solid Na_2CO_3 (5.3 g, 50.0 mmol) and As_2O_3 (2.5 g, 10.0 mmol) were added. Upon complete dissolution of the solids, $CuSO_4·5H_2O$ (0.11 g, 0.44 mmol) was added. The resulting blue solution was allowed to cool to room temperature and then cooled to 0 °C (solution 2). Solution 1 was added dropwise to solution 2 at 0 °C over a period of 1 h under continuous high-speed stirring. A strong effervescence was observed because of the release of N_2 gas from the intermediate diazonium salt as the reaction proceeded. When the addition was complete, the reaction mixture was kept for 2 h at room temperature under constant stirring. The resulting orange solution was filtered, and the colorless filtrate was collected. The filtrate was adjusted to pH 7 with concentrated HCl and then filtered again. Subsequently, the filtrate was adjusted to pH 1 with concentrated HCl to obtain a colorless precipitate. The pH adjustments were accompanied by an effervescence. The solution was left overnight at 4 °C, and then the precipitate was filtered, washed with water, and dried in air. Yield: 4.78 g (85%). IR (2% KBr pellet, ν/cm^{-1}): 1571 (sh), 1474 (sh), 1386 (sh), 1253 (m), 1208 (s), 1091 (s), 1064 (sh), 1009 (m), 901 (w), 810 (s), 786 (s), 761 (m), 711 (s), 485 (m), 435 (s). ^1H NMR (400 MHz, DMSO-d^6): δ 7.64 (d, 2H, Ar), 7.81 (d, 2H, Ar), ^{13}C NMR (400 MHz, DMSO-d^6): δ 127.6, 131.1, 132.3, 133.1.

$((NH_2)_3C)_4[(BrC_6H_4As)_2Mo_6O_{24}]·2H_2O$ ***(Gua-$Mo_6As_2L_a$).*** $Na_2MoO_4·2H_2O$ (0.774 g, 3.20 mmol) and $BrC_6H_4AsO_3H_2$ (0.280 g, 1.00 mmol) were dissolved in 5 mL of water at room temperature. The pH of the reaction mixture was adjusted to 3.5 by adding 6 M H_2SO_4, followed by reflux for 1 h. The reaction mixture was then filtered, and the filtrate, upon cooling to room temperature, was added to an aqueous solution of guanidium chloride at pH 3.5 [prepared by dissolving 0.122 g of $(NH_2)_3CCl$ in 20 mL of water and adjusting the pH with diluted H_2SO_4]. This mixture was then heated at 80 °C until the volume had reduced to 15 mL. Upon cooling to room temperature, colorless block-shaped crystals of **Gua-$Mo_6As_2L_a$** were formed that were filtered off and air-dried. Yield: 0.60 g (70% based on Mo). Elem anal. Calcd for **Gua-$Mo_6As_2L_a$**: Mo, 33.90; As, 8.83; Br, 9.41; C, 11.32; H, 2.14; N, 9.90. Found: Mo, 34.28; As, 8.47; Br, 9.24; C, 10.92; H, 2.06; N, 10.30. IR (2% KBr pellet, ν/cm^{-1}): 1423 (s), 1421 (sh), 1383 (s), 1330 (s), 1321 (sh), 1043 (m), 1020 (m), 925 (w), 701 (sh), 689 (s), 650 (s), 617 (w), 602 (w), 518 (w), 501 (w).

$((NH_2)_3C)_4[(N_3C_6H_4As)_2Mo_6O_{24}]$ ***(Gua-$Mo_6As_2L_b$).*** Polyanion **$Mo_6As_2L_b$** was synthesized using the same procedure as that for **$Mo_6As_2L_a$** but by using (4-azidophenyl)arsonic acid, $N_3C_6H_4AsO_3H_2$ (0.243 mg, 1.00 mmol),[3a] instead of (4-bromophenyl)arsonic acid. Yield: 0.64 mg (75% based on Mo). Elem anal. Calcd for **Gua-$Mo_6As_2L_b$**: Mo, 36.29; As, 9.45; C, 12.12; H, 2.03; N, 15.90. Found: Mo, 36.35; As, 9.64; C, 11.88; H, 2.03; N, 15.76. IR (2% KBr pellet, ν/cm^{-1}): 1423 (s), 1421 (sh), 1383 (s), 1330 (s), 1321 (sh), 1043 (m), 1020 (m), 925 (w), 701 (sh), 689 (s), 650 (s), 617 (w), 602 (w), 518 (w), 501 (w).

$Rb_3Na_3[(O_2CC_6H_4P)_2Mo_5O_{21}]·5H_2O$ ***(RbNa-$Mo_5P_2L_c$).*** $Na_2MoO_4·2H_2O$ (0.30 g 1.25 mmol) was dissolved in 15 mL of water, followed by the addition of (4-carboxyphenyl)phosphonic acid ($HO_2CC_6H_4PO_3H_2$; 0.10 g, 0.50 mmol) and KCl (0.11 g, 1.50 mmol). The reaction mixture was stirred at room temperature for 15 min, and then the pH of the clear solution was adjusted from 6 to 3 by adding concentrated HCl(aq). Subsequently, the reaction mixture was refluxed for 30 min. After the solution was cooled to room temperature, 0.8 g of solid RbCl was added and dissolved by stirring. The solution was then filtered into a 20 mL beaker, which was placed in a larger flask containing some ethanol. The larger flask was closed with a lid, and diffusion of ethanol vapor into the reaction solution led to the formation of colorless crystals of **RbNa-$Mo_5P_2L_c$** after a few days, which were filtered off and air-dried. Yield: 0.30 g (80% based on Mo). Elem anal. Calcd for **RbNa-$Mo_5P_2L_c$**: Rb, 16.72; Na, 4.50; Mo, 31.29; P, 4.04; C, 10.97; H, 1.18. Found: Rb, 17.12; Na, 4.29; Mo, 31.38; P, 4.24; C, 10.55; H, 1.26. IR (2% KBr pellet, ν/cm^{-1}): 1423 (s), 1421 (sh), 1383 (s), 1330 (s), 1321 (sh), 1043 (m), 1020

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Table 1. Crystal Data and Structure Refinement for **Gua-$Mo_6As_2L_a$**, **Gua-$Mo_6As_2L_b$**, **RbNa-$Mo_5P_2L_c$**, and **CsK-$Mo_5P_2L_d$**

	Gua-$Mo_6As_2L_a$	Gua-$Mo_6As_2L_b$	RbNa-$Mo_5P_2L_c$	CsK-$Mo_5P_2L_d$
empirical formula[a]	$C_{16}H_{32}As_2Br_2N_{12}Mo_6O_{24}$ ($C_{16}H_{36}As_2Br_2N_{12}Mo_6O_{26}$)	$C_{16}H_{32}As_2N_{18}Mo_6O_{24}$	$C_{14}H_8Mo_5Na_2O_{29}P_2Rb_3$ ($C_{14}H_{18}Mo_5Na_3O_{30}P_2Rb_3$)	$C_{16}H_8Cs_3Mo_5O_{31}P_2$ ($C_{16}H_{24}Cs_3KMo_5O_{30}P_2$)
fw,[a] g mol^{-1}	1661.83 (1697.81)	1586.07	1484.23 (1533.29)	1636.59 (1675.80)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2(1)/n$	$P2(1)/n$	$P2(1)/c$	$C2/c$
a, Å	10.4611(10)	10.4029(18)	18.2365(15)	13.5121(16)
b, Å	18.3773(16)	18.112(3)	12.8646(10)	15.3292(18)
c, Å	12.2541(10)	12.347(2)	15.2918(13)	21.896(3)
α, deg	90	90.00	90	90
β, deg	108.029(4)	106.449(7)	103.492(2)	101.695(3)
γ, deg	90	90.00	90	90
volume, $Å^3$	2240.1(3)	2231.2(7)	3488.5(5)	4441.3(9)
Z	2	2	4	4
D_{calc}, g cm^{-3}	2.464	2.361	2.826	2.448
abs coeff, mm^{-1}	4.969	3.207	6.130	3.959
$F(000)$	1584.0	1528	2788	3028
θ range for data collection, deg	2.823−27.648	2.530−27.587	1.956−27.489	2.657−27.545
completeness to Θ_{max}, %	99.4	99.4	99.7	99.7
index ranges	$-13 \le h \le 13, -22 \le k \le 23, -15 \le l \le 15$	$-13 \le h \le 13, -23 \le k \le 23, -16 \le l \le 16$	$-23 \le h \le 23, -16 \le k \le 13, -11 \le l \le 19$	$-17 \le h \le 17, -19 \le k \le 19, -28 \le l \le 28$
reflns collected	22007	24434	22440	41052
indep reflns	5176	5134	7956	5118
R(int)	0.0682	0.0641	0.0527	0.0411
abs corrn	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents
data/restraints/param	5176/13/289	5134/0/298	7956/258/499	5118/114/272
GOF on F^2	1.044	1.150	1.036	1.182
R_1,[b] wR_2[c] [$I > 2\sigma(I)$]	R_1 = 0.0405, wR_2 = 0.0992	R_1 = 0.0429, wR_2 = 0.1145	R_1 = 0.0391, wR_2 = 0.0823	R_1 = 0.0701, wR_2 = 0.1765
R_1,[b] wR_2[c] (all data)	R_1 = 0.0512, wR_2 = 0.1049	R_1 = 0.0469, wR_2 = 0.1193	R_1 = 0.0559, wR_2 = 0.0882	R_1 = 0.0769, wR_2 = 0.1806
largest diff peak and hole, e $Å^{-3}$	1.558 and −1.954	1.070 and −1.164	3.072 and −1.612	4.604 and −1.428

[a] The entries in parentheses are the actual formula units and weights as obtained from elemental analysis. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

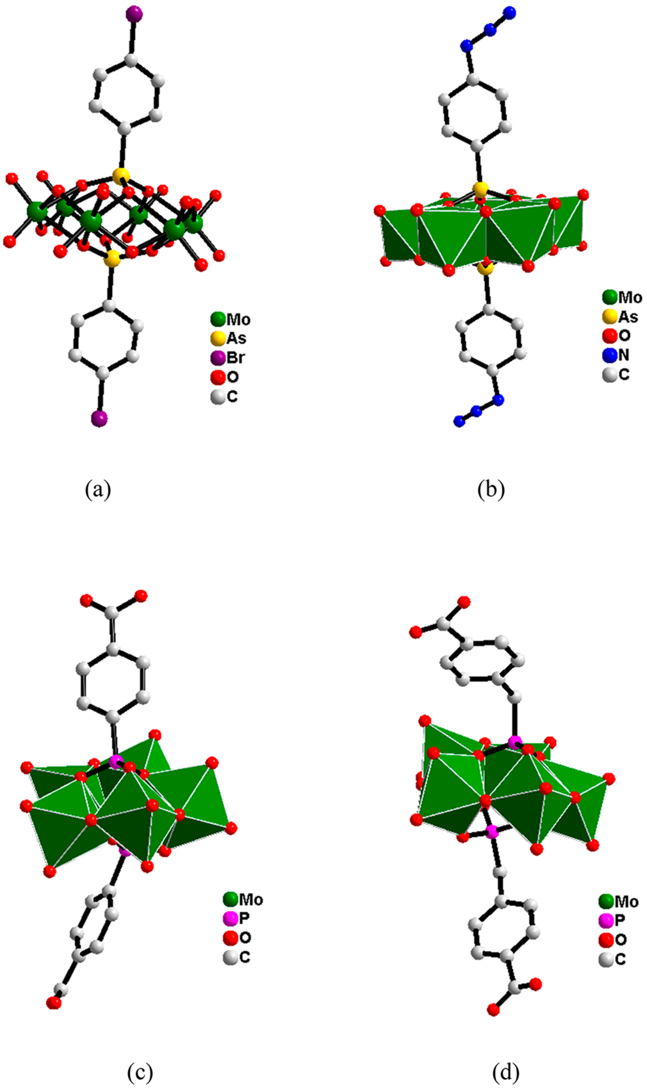
(m), 925 (w), 701 (sh), 689 (s), 650 (s), 617 (w), 602 (w), 518 (w), 501 (w).

*$Cs_3K[(HO_2CC_6H_4CH_2P)_2Mo_5O_{21}]\cdot 5H_2O$ (**CsK-$Mo_5P_2L_d$**).* The polyanion **$Mo_5P_2L_d$** was synthesized by the same procedure as that used for **$Mo_5P_2L_c$** but by using (4-carboxybenzyl)phosphonic acid ($HO_2CC_6H_4CH_2PO_3H_2$; 0.108 g, 0.500 mmol) instead of (4-carboxyphenyl)phosphonic acid. The reaction mixture was left at room temperature in an open container for crystallization, and after 3 days, colorless crystals were obtained in roughly 30% yield (no elemental analysis was performed on this material, but on the basis of IR, it is clean **$Mo_5P_2L_d$** as a hydrated potassium−sodium salt). The yield of the polyanion **$Mo_5P_2L_d$** could be increased significantly by adding 0.5 g of solid CsCl to the reaction mixture after it had cooled to room temperature and then keeping the 20 mL beaker inside a larger, capped container with ethanol, analogously to **$Mo_5P_2L_c$**. After 2 days, colorless crystals of **CsK-$Mo_5P_2L_d$** were obtained. Yield: 0.32 g (78% based on Mo). Using RbCl (as for the synthesis of **$Mo_5P_2L_c$**) instead of CsCl resulted in the immediate formation of a colorless precipitate (which was not further analyzed). Elem anal. Calcd for **CsK-$Mo_5P_2L_d$**: Cs, 22.58; K, 2.21; Mo, 27.16; P, 3.51; C, 10.88; H, 1.94. Found: Cs, 22.37; K, 2.42; Mo, 27.17; P, 3.41; C, 10.19; H, 1.57. IR (2% KBr pellet, ν/cm^{-1}): 1423 (s), 1421 (sh), 1383 (s), 1330 (s), 1321 (sh), 1043 (m), 1020 (m), 925 (w), 701 (sh), 689 (s), 650 (s), 617 (w), 602 (w), 518 (w), 501 (w).

X-ray Crystallography. Single crystals of **RbNa-$Mo_5P_2L_a$**, **CsK-$Mo_5P_2L_b$**, **Gua-$Mo_6As_2L_c$**, and **Gua-$Mo_6As_2L_d$** were mounted on a Hampton cryoloop with light oil, and then data were collected on a Bruker Kappa X8 APEX II CCD diffractometer with a sealed Mo tube and a graphite monochromator using Kα radiation (λ = 0.71073 Å) at 100 K. An empirical absorption correction was applied using the *SADABS* program.[15] The *SHELX* software package (Bruker) was used to solve and refine the structures.[16] The structures were solved by direct methods and refined by the full-matrix least-squares method ($\sum w(|F_o|^2 - |F_c|^2)^2$) with anisotropic thermal parameters for all heavy atoms included in the model. Hydrogen atoms on the carbon atoms were introduced in calculated positions and included in the refinement riding on their respective parent atoms. It was impossible to locate all sodium countercations via Fourier electron density because of crystallographic disorder, which is a common problem in POM crystallography, and the most disagreeable reflections were removed by the *SQUEEZE* command in *PLATON*.[17] Therefore, the true number of countercations and crystal water molecules in the compounds was determined by elemental analysis, and the resulting formula units were used throughout the paper and in the CIF file for overall consistency. The crystal data and structure refinement parameters for the four compounds are summarized in Table 1. Images of the crystal structures were generated by *Diamond*, version 3.2 (software copyright, Crystal Impact GbR). The data are provided free of charge by The Cambridge Crystallographic Data Centre via the deposition codes CCDC 2034543−2034546.

■ RESULTS AND DISCUSSION

Over the years, some organoarsonate-capped polyoxomolybdates have been reported, such as the tetranuclear polyanion $[(O_3AsR)_4Mo_4O_{10}]^{4-}$ [18a,b] and the dodecanuclear polyanion $[(O_3AsR)_4Mo_{12}O_{34}]^{4-}$ (R = Ph, MeC_6H_4, 4-$NH_2C_6H_4$, C_2H_4OH, 4-HOC_6H_4, 4-$HO_2CC_6H_4$, 3-O_2N,4-HOC_6H_3, 4-NCC_6H_4, 3-C_2H_4ON, 4-HOC_6H_3).[18] The hexanuclear polyanion $[(O_3AsR)_2Mo_6O_{18}]^{4-}$ (R = CH_3, Ph, 4-$NH_2C_6H_4$) was reported by Pope's group in 1976,[11] and Liu et al. reported an additional derivative (R = n-C_3H_7) in 1988.[12] To date, no further derivatives of this hexamolybdate structure have been reported.



(a) (b)

(c) (d)

Figure 1. Combined polyhedral/ball-and-stick representation of (a) **$Mo_6As_2L_a$**, (b) **$Mo_6As_2L_b$**, (c) **$Mo_5P_2L_c$**, and (d) **$Mo_5P_2L_d$**. Color code: MoO_6 octahedra, green; As, yellow; P, pink; O, red; Br, violet; N, blue; C, gray. No hydrogen atoms are shown for clarity.

The reaction of (4-bromophenyl)arsonic acid with sodium molybdate in an aqueous pH 3−3.5 solution at 1 h reflux conditions resulted in $[(BrC_6H_4As)_2Mo_6O_{24}]^{4-}$ (**$Mo_6As_2L_a$**) in 70% yield (Figure 1a). The novel polyanion **$Mo_6As_2L_a$** was isolated as a hydrated guanidinium salt, **Gua-$Mo_6As_2L_a$**, which crystallized in the monoclinic system with the $P2_1/n$ space group (Table 1). The six edge-shared MoO_6 octahedra form a ring, which is capped on each side by a (4-bromophenyl)-arsonate group. Polyanion **$Mo_6As_2L_a$** exhibits (i) terminal oxygen atoms with Mo−O bond lengths in the range of 1.702−1.715(5) Å, (ii) doubly bridging oxygen atoms with Mo−O(Mo) bond lengths in the range of 1.894−1.937(5) Å, and (iii) triply bridging oxygen atoms with Mo−O(As) bond lengths in the range of 2.278−2.343(5) Å. The arsenic atoms exhibit a tetrahedral geometry with O−As−O bond angles in the range of 108.96−110.65(4)° and As−O bond lengths from 1.687 to 1.815(7) Å, as well as As−C bond lengths of 1.896−2.142(8) Å. In the solid state, individual polyanions **$Mo_6As_2L_a$** are surrounded by four guanidinium cations and two water molecules, leading to the formula unit $((NH_2)_3C)_4[(BrC_6H_4As)_2Mo_6O_{24}]\cdot 2H_2O$ (**Gua-$Mo_6As_2L_a$**), which represents a 3D network stabilized by hydrogen bonding of the guanidinium cations with oxygen atoms of the polyanion.

The reaction of (4-azidophenyl)arsonic acid (**$N_3C_6H_4AsO_3H_2$**; prepared according to ref 3a; see the Experimental Section for details) with sodium molybdate under the same conditions as those used for the synthesis of **$Mo_6As_2L_a$** resulted in the novel polyanion $[(N_3C_6H_4As)_2Mo_6O_{24}]^{4-}$ (**$Mo_6As_2L_b$**; Figure 1b). The structure of **$Mo_6As_2L_b$** is identical with that of **$Mo_6As_2L_a$** except for the para substituent of the phenyl ring, which is N_3 in the former and Br in the latter. Hence, the Mo−O and As−O/As−C bond lengths in **$Mo_6As_2L_b$** and **$Mo_6As_2L_a$** are very similar. Furthermore, **Gua-$Mo_6As_2L_a$** is isomorphous with **Gua-$Mo_6As_2L_b$**, and hence they exhibit identical 3D solid-state assemblies.

Being inspired by the previous results on arsonate-capped polyoxomolybdates, we decided to also study organophosphonate-containing capping groups with molybdate ions in an aqueous acidic solution.

The reaction of (4-carboxybenzyl)phosphonic acid with sodium molybdate in an aqueous pH 3 solution for a 30 min reflux resulted in $[(O_2CC_6H_4P)_2Mo_5O_{21}]^{6-}$ (**$Mo_5P_2L_c$**) in 80% yield (Figure 1c). The novel polyanion **$Mo_5P_2L_c$** was isolated as a hydrated mixed rubidium−sodium salt, **RbNa-$Mo_5P_2L_c$**, which crystallized in the monoclinic system with the $P2_1/c$ space group (Table 1). The five MoO_6 octahedra in **$Mo_5P_2L_c$** are shared by a total of four edges and one corner, forming a ring that is capped on each side by a (4-carboxyphenyl)-phosphonate group (Figure 1c). This structure can be considered to be the aryl analogue of our earlier-reported $[(O_2CCH_2PO_3)_2Mo_5O_{15}]^{6-}$.[10]

In **$Mo_5P_2L_c$**, the two carboxylate groups of (4-carboxyphenyl)phosphonic acid remain deprotonated in the polyanion structure, with one of them being weakly coordinated to a Na^+ ion ($Na\cdots O_C$ = 2.21 Å) and the other to a Rb^+ ion ($Rb\cdots O_C$ = 2.92 Å). In total, there are three sodium and three rubidium ions balancing the negative charge of each polyanion **$Mo_5P_2L_c$**. The countercations interact with terminal oxygen atoms of $\{Mo_5O_{21}\}$ units as well as crystal water molecules, resulting in an overall 3D supramolecular arrangement in the solid state. Good-quality single crystals of polyanion **$Mo_5P_2L_c$** in decent yield were obtained in the presence of rubidium cations using the ethanol vapor diffusion technique. We discovered that the presence of K^+ ions during the synthesis allowed one to isolate the polyanion **$Mo_5P_2L_c$** in better yield, although no potassium ions could be detected in the final product **RbNa-$Mo_5P_2L_c$**. It is not evident what role K^+ ions play during the formation and/or crystallization process of **$Mo_5P_2L_c$**.

The reaction of (4-carboxybenzyl)phosphonic acid with sodium molybdate under identical conditions as those for the synthesis of **$Mo_5P_2L_c$** resulted in $[(HO_2CC_6H_4CH_2P)_2Mo_5O_{21}]^{4-}$ (**$Mo_5P_2L_d$**) in 78% yield (Figure 1d). The novel polyanion **$Mo_5P_2L_d$** was isolated as a hydrated mixed cesium−potassium salt, **CsK-$Mo_5P_2L_d$**, which crystallized in the monoclinic system with the $C2/c$ space

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group (Table 1). Overall, the structure of $\mathbf{Mo_5P_2L_d}$ is identical with that of $\mathbf{Mo_5P_2L_c}$, except that the phosphonate capping group of the former has an extra degree of freedom because of the methylene (CH_2) group, which allows the planar aryl group to move about a large cone angle and rotate at the same time, whereas the aryl group in $\mathbf{Mo_5P_2L_c}$ can only rotate around the P−C bond. The P−C−C angle for $\mathbf{Mo_5P_2L_d}$ in the solid state is ca. 112°, whereas the P−C vector in $\mathbf{Mo_5P_2L_c}$ can only rotate. It should be noted that $\mathbf{Mo_5P_2L_c}$ is fully deprotonated, whereas $\mathbf{Mo_5P_2L_d}$ has both carboxylate groups protonated, although both are synthesized at pH 3, which leads to a charge difference of two units between the two polyanions. It is likely that different solid-state packing effects are responsible for this phenomenon, considering that both polyanions have different countercations and crystallize in different space groups.

NMR SPECTROSCOPY

The ^{31}P NMR spectra for **RbNa-**$\mathbf{Mo_5P_2L_c}$ and **CsK-**$\mathbf{Mo_5P_2L_d}$ were collected in H_2O/D_2O at pH 3. The former exhibits a singlet at 19.5 ppm, whereas the latter exhibits a singlet at 28.1 ppm (Figure 2). At the same pH, the free capping groups (4-carboxyphenyl)phosphonic acid and (4-carboxybenzyl)-phosphonic acid exhibit chemical shifts at 12.4 and 20.1 ppm, respectively. These results confirm the solution stability of both polyanions $\mathbf{Mo_5P_2L_c}$ and $\mathbf{Mo_5P_2L_d}$.

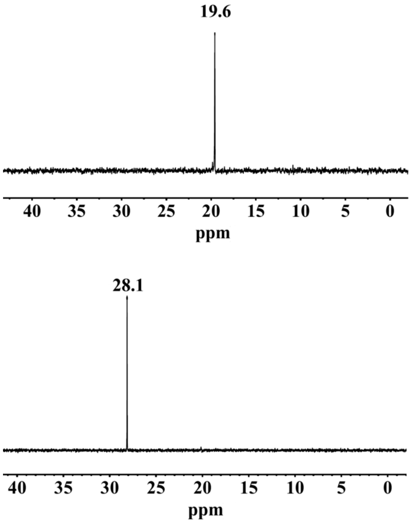

Figure 2. ^{31}P NMR spectra of solid **RbNa-**$\mathbf{Mo_5P_2L_c}$ (top) and **CsK-**$\mathbf{Mo_5P_2L_d}$ (bottom) dissolved in water at pH 3.

We also performed some control reactions at different synthetic conditions monitored by ^{31}P NMR to better understand the formation mechanism of the polyanions $\mathbf{Mo_5P_2L_c}$ and $\mathbf{Mo_5P_2L_d}$ from the respective starting materials (Figure 3). The capping group for $\mathbf{Mo_5P_2L_c}$ as a free acid is $HO_2CC_6H_4PO_3H_2$, which exhibits a singlet in the ^{31}P NMR spectrum at 12.9 ppm in water at pH 6. The reaction mixture of $Na_2MoO_4{\cdot}2H_2O$, $HO_2CC_6H_4PO_3H_2$, and KCl in water (pH 6) results in two peaks at 12.9 and 20.3 ppm, corresponding to the free phosphonic acid and polyanion $\mathbf{Mo_5P_2L_c}$, respectively. Such an observation indicates that the self-assembly of $\mathbf{Mo_5P_2L_c}$ takes place already at room temperature after mixing the starting materials in water (resulting in pH 6), but there is still a significant amount of free phosphonic acid present at such a pH. After adjustment to pH 3 by concentrated HCl(aq) and stirring at room temperature for 30 min, the reaction mixture showed a clean singlet at 19.6 ppm, corresponding to the polyanion $\mathbf{Mo_5P_2L_c}$. Reflux of the reaction mixture for 20 min at pH 3 also resulted in a clean ^{31}P NMR spectrum with a singlet at 19.6 ppm. Furthermore, a very short 5 min reaction in a microwave at 70 °C also resulted in a clean singlet at 19.6 ppm, indicating the smooth formation of $\mathbf{Mo_5P_2L_c}$. We also performed a solid-state reaction by simple mixing and grinding of the solid reagents $Na_2MoO_4{\cdot}2H_2O$, $HO_2CC_6H_4PO_3H_2$, and KCl in a mortar, followed by dissolution in water (pH 6), which gave two peaks at 12.9 and 20.3 ppm, respectively, in analogy to the reaction mixture in aqueous solution at pH 6 as described above. All of these results confirm that the polyanion $\mathbf{Mo_5P_2L_c}$ is formed easily and cleanly in a pH 3 aqueous solution.

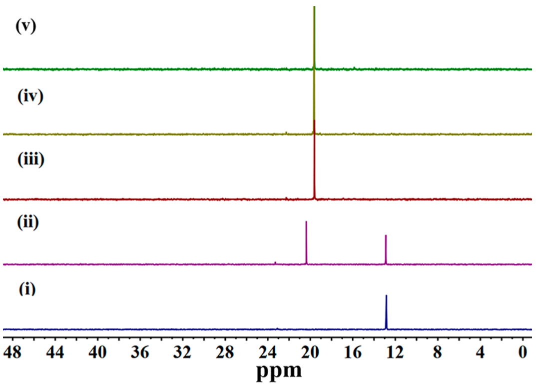

Figure 3. ^{31}P NMR spectra of $\mathbf{Mo_5P_2L_c}$ at different reaction conditions: (i) free ligand $HO_2CC_6H_4PO_3H_2$ at pH 6; (ii) reaction mixture of $Na_2MoO_4{\cdot}2H_2O$, $HO_2CC_6H_4PO_3H_2$ and KCl in water at pH 6; (iii) reaction mixture after pH adjustment to pH 3 and 30 min of stirring at room temperature; (iv) reaction mixture after 20 min of reflux (pH 3); (v) reaction mixture after 5 min of microwave heating at 70 °C (pH 3).

CONCLUSIONS

We report on the synthesis and structural characterization of $BrC_6H_4AsO_3H_2$ for the first time. When reacting $BrC_6H_4AsO_3H_2$ with sodium molybdate in an aqueous acidic medium, we obtained the bicapped hexamolybdate $\mathbf{Mo_6As_2L_a}$. When the same reaction was performed with $N_3C_6H_4AsO_3H_2$ as the capping group, then the polyanion $\mathbf{Mo_6As_2L_b}$ was formed. Both polyanions $\mathbf{Mo_6As_2L_b}$ and $\mathbf{Mo_6As_2L_a}$ are isostructural, comprising a cyclic core of six edge-shared MoO_6 octahedra with two capping groups attached on opposite sides.

The reaction of two arylphosphonates (RPO_3, where R = 4-$O_2CC_6H_4$ and 4-$O_2CC_6H_4CH_2$) with sodium molybdate in aqueous acidic media resulted in the cyclic pentamolybdates $\mathbf{Mo_5P_2L_c}$ and $\mathbf{Mo_5P_2L_d}$, respectively, which are capped on either side by a arylphosphonate group. The ^{31}P NMR spectra for $\mathbf{Mo_5P_2L_c}$ and $\mathbf{Mo_5P_2L_d}$ exhibit singlets at 19.5 and 28.1 ppm, respectively, indicating that both polyanions are solution-stable. In 2003, our group reported the first example of a 5-molybdo-2-phosphonate functionalized with aliphatic phosphonocarboxylates, $[(O_2C(CH_2)_nPO_3)_2Mo_5O_{21}]^{6-}$ (n = 1, 2), respectively. The polyanions $\mathbf{Mo_5P_2L_c}$ and $\mathbf{Mo_5P_2L_d}$ presented here are the first examples of Strandberg-type polyanions with carboxyphenylphosphonate capping groups.

Our work demonstrates that the size of the heteroatom X (X = P, As) and the corresponding X−O bond length differences (P−O ∼ 1.5 Å vs As−O ∼ 1.7 Å) determine which POM structure type is formed. For the two arylarsonate hetero groups, cyclic hexamolybdates are formed, with a ring size accommodating the longer As−O bonds, whereas for the two arylphosphonate hetero groups, cyclic pentamolybdates are formed, providing a ring size suitable for the shorter P−O bonds.

For all four polyanions **$Mo_6As_2L_a$**, **$Mo_6As_2L_b$**, **$Mo_5P_2L_c$**, and **$Mo_5P_2L_d$**, the functional groups in the para position of the aryl groups (e.g., $-N_3$, −Br, −COOH) can, in principle, be further covalently conjugated to biomolecules (e.g., peptides, nucleotides, antibodies, nanoparticles), thereby increasing the capability of these materials for use in biomedical applications. Our future work on such types of polyanions is geared in this direction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00245.

Molecular structures of the arylarsonate and -phosphonate precursors, NMR (^{1}H, ^{13}C) and FTIR spectra, and thermograms (PDF)

Accession Codes

CCDC 2034543−2034546 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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Notes

The authors declare no competing financial interest.

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DEDICATION

Dedicated to Prof. Imre Tóth on the occasion of his 70th birthday.

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