ABSTRACT: Functionalization of the \{P_{n}W_{4n}\} polyanion (POT) archetype with aromatic organoarsonates results in the first homometallic \{P_{n}W_{4n}\} derivatives, with the general formula \{(RAsO\_V)\_nMo\_VI\_n\_O\_18\_x\_H\_x\}^{2\_n\_−}\ [R = C\_6H\_4 (1) or \(p\)-(H\_2N\_C\_6H\_4\_Ch\_2) (2)]. Short As−O bonds here induce unusual bending of the otherwise rigid \{P_{n}W_{4n}\} macrocycle, breaking its \(D_{4h}\) symmetry. The obtained species also represent the first lacunary POTs functionalized with organoarsonates and can potentially act as polyoxometalate precursors themselves. We elaborate solution stability in different aqueous media using \(^1\)H and \(^31\)P NMR spectroscopy and possible pathways for subsequent transformations in aqueous solutions of the functionalized polyanions. Recrystallization of the \(K^\_7/Li^\_7/dimethylammonium\) salt of \{P_{8}W_{48}\} from 4 M LiCl solution yielded a further functionalized POT, \[(H\_3NC\_6H\_4AsO)\_3P\_8W\_48O\_18\_4\_H\_2\]^{3\_−}\ (3), revealing dissociation of the organoarsonate fragments in slightly acidic aqueous solutions followed by their rearrangement within the inner POT cavity.

1. INTRODUCTION

The combination of structural versatility, redox robustness, and the ability to act as multidentate ligands toward oxophilic heterometals renders polyanions (POTs), a large family of discrete polynuclear oxo complexes of \(W^{VI}\) and \(W^{IV}\) ions, highly attractive for application in many areas ranging from catalysis, electrochemistry, photochromism, and magnetism to medicine. Further extension of these clusters’ structural diversity can be achieved by their functionalization with organic moieties, e.g., organosilyl, organophosphonate and -phosphoryl, organotin, and other groups.

Until now, the reactivity of organoarsenic-based reagents toward POTs has received relatively little attention. While a series of organoarsinates \([RAs\_V\_O\_3Mo\_VI\_n\_O\_3\_H\_x]\) \(\{R = \text{CH}_3, \text{C}_6\text{H}_5, \text{C}_2\text{H}_5\}\) and organoarsonate-functionalized polyoxymolybdates with formulas \([\{(RAsO\_V)\_nMo\_VI\_n\_O\_18\_x\_H\_x\}\]^{2\_n\_−}\) \([\text{MeAsO}\_V\_O\_3Mo\_VI\_n\_O\_3\_H\_x]\)^{2\_n\_−}\) \([\{(RAsO\_V)\_2Mo\_VI\_n\_O\_18\_x\_H\_x\}\]^{2\_n\_−}\) \([\{(RAsO\_V)\_3Mo\_VI\_n\_O\_18\_x\_H\_x\}\]^{2\_n\_−}\) \([\{(RAsO\_V)\_4Mo\_VI\_n\_O\_18\_x\_H\_x\}\]^{2\_n\_−}\) \(\{(\text{PhAsO}\_V\_O)\_Mo\_VI\_n\_O\_18\_x\_H\_x\}^{2\_n\_−}\) \(\{(RAsO\_V)\_Mo\_VI\_n\_O\_18\_x\_H\_x\}^{2\_n\_−}\) \(\{(RAsO\_V)\_Mo\_VI\_n\_O\_18\_x\_H\_x\}^{2\_n\_−}\) \(\{(RAsO\_V)\_Mo\_VI\_n\_O\_18\_x\_H\_x\}^{2\_n\_−}\) \(\{(RAsO\_V)\_Mo\_VI\_n\_O\_18\_x\_H\_x\}^{2\_n\_−}\) \(\{(RAsO\_V)\_Mo\_VI\_n\_O\_18\_x\_H\_x\}^{2\_n\_−}\) \(\{(RAsO\_V)\_Mo\_VI\_n\_O\_18\_x\_H\_x\}^{2\_n\_−}\) \(\{(RAsO\_V)\_Mo\_VI\_n\_O\_18\_x\_H\_x\}^{2\_n\_−}\) \(\{(RAsO\_V)\_Mo\_VI\_n\_O\_18\_x\_H\_x\}^{2\_n\_−}\) \(\{(RAsO\_V)\_Mo\_VI\_n\_O\_18\_x\_H\_x\}^{2\_n\_−}\) explored the reactivity of organoarsonates with multilacunary POTs. The seminal, highly stable macrocyclic POT \([H\_8P\_8W\_48O\_18\_4\_H\_2]\]^{3\_−}\) \(\{(P\_8W\_48)\}^{6}\) was chosen for these experiments because it is regarded as highly stable and comparably inert toward substitution of its phosphate heterogroups and provides adequate coordination sites between its four \{P\_8W\_48\} building blocks. In \{P\_8W\_48\}, the latter are linked by oxo bridges into a wheel-shaped structure with a large inner cavity (approximately 1 nm in diameter), able to accommodate various transition and rare-earth metals as well as their oxo/hydroxo clusters, e.g., in \([\text{Cu}(\text{OH})\_3(\text{H}_2\text{O})\_3]P\_8W\_48O\_18\_4\_H\_2\]^{2\_−}\) \((X = \text{Cl, Br}, 1)\), \([\text{Cu}(\text{OH})\_3P\_8W\_48O\_18\_4\_H\_2\]^{2\_−}\) \(\{(\text{HOSn}\_II\_P}\_8W\_48O\_18]\]^{−}\) and \([\text{K}_8C(P\_8W\_48O\_18\_4[\text{Mo}^{V}\_O\_3]\_4\[\text{Mo}^{V}\_O\_10(\text{H}_2\text{O})\]_3]\]^{2\_−}\). More over, it can act as a secondary building block in numerous fully inorganic coordination polymers, as exemplified by the 3D framework compounds \(K\_8Li\_7[\text{Mn}(\text{H}_2\text{O})\_4]P\_8W\_48O\_18\_4\_H\_2\]^{10\_+}\) with huge rigid voids or the recently reported \(\text{Li}_4K\_8W\_48O\_18\_4[\text{H}_2\text{O}\]_{16}\_n\]H\_2\text{O}, which can undergo several crystal-to-crystal transformations, resulting in structures of different connectivities (from 0D up to 3D). An additional advantage of \{P\_8W\_48\} as the precursor for further functionalization is its solubility and stability in aqueous solutions in the unusually broad pH range from 1 to 8.

Very recently, we have reported the first examples of \{P\_8W\_48\} complexes with the main-group metals \([\text{K}_4.5\_S\_C(\text{ClSn}\_II\_P}\_8W\_48O\_18\_4\_H\_2\]^{17\_−}\) and \([\text{HO}(\text{Sn}\_II\_P}\_8W\_48O\_18\_4\_H\_2\]^{17\_−}\). At the same time, to our knowledge, no \{P\_8W\_48\}
derivatives with nonmetal elements are known. We here report two \( ([\text{RaSbO}_3])_2P_4\text{W}_{18}\text{O}_{61})_\text{in} \) \(^{31}\)P magic-angle-spinning (MAS) NMR measurements were performed at a cycle delay of 120 s was used. The signal of 35 and 15 kHz were applied during MAS. The 8-fold cyclization of pH 2.2 adjusted by glacial acetic acid was added dropwise to a solution of \( \text{C}_{38}\text{H}_{33}\text{As}_4\text{K}_8\text{Li}_{17}\text{N}_7\text{O}_{31}\text{P}_8\text{W}_{48} \) (found), mass %: C, 2.89 (2.90); H, 2.15 (2.25); As, 1.90 (1.94); K, 1.99 (1.85); Li, 0.64 (0.62); N, 0.70 (0.77); P, 1.64 (1.62); W, 58.52 (58.02). IR (KBr pellets, cm\(^{-1}\)) = 3422 (s, br), 1629 (s), 1496 (w), 1465 (w), 1413 (w), 1324 (w), 1135 (m), 1085 (m), 1023 (m), 935 (s), 833 (s), 728 (s), 671 (s), 464 (s). The crystals were collected by filtration and dried in air. Yield: 0.15 g (41 % based on \( P_\text{W}_{18} \)). E:men a. Calculated for \( \text{C}_{38}\text{H}_{33}\text{As}_4\text{K}_8\text{Li}_{17}\text{N}_7\text{O}_{31}\text{P}_8\text{W}_{48} \) (found), mass %: C, 2.47 (2.46); H, 1.60 (1.59); As, 1.99 (1.85); K, 2.72 (2.68); Li, 0.64 (0.62); N, 0.70 (0.77); P, 1.64 (1.62); W, 58.52 (58.02). IR (KBr pellets, cm\(^{-1}\)) = 3440 (s, br), 1629 (s), 1497 (w), 1416 (w), 1326 (w), 1294 (w), 1135 (m), 1083 (m), 1022 (m), 937 (s), 816 (s), 677 (s), 464 (s). Raman (solid sample, cm\(^{-1}\)) = 969 (s), 890 (m), 801 (w), 695 (m), 633 (m), 570 (m), 320 (w), 207 (m). 2.2. Synthesis of KL-4. A sample of KL-4 (0.040 g, 0.003 mmol) was dissolved in aqueous 4 M LiCl (22 mL), followed by the addition of FeCl\(_3\)·6H\(_2\)O (0.006 g, 0.021 mmol), while the reaction mixture was stirred at 70 °C for 40 min. After that, the solution (pH 2.7) was divided into four vials and left for evaporation at room temperature. Needlelike crystals of KL-3 started to form after 1 week. The crystals were collected by filtration and dried in air. Yield: 0.021 g. IR (KBr pellets, cm\(^{-1}\)) = 3440 (s, br), 1629 (s), 1497 (w), 1416 (w), 1326 (w), 1294 (w), 1135 (m), 1083 (m), 1022 (m), 937 (s), 816 (s), 677 (s), 464 (s). Raman (solid sample, cm\(^{-1}\)) = 969 (s), 890 (m), 801 (w), 695 (m), 633 (m), 570 (m), 320 (w), 207 (m). 2.2. Synthesis of KL-4. A sample of KL-4 (0.040 g, 0.003 mmol) was dissolved in aqueous 4 M LiCl (22 mL), followed by the addition of FeCl\(_3\)·6H\(_2\)O (0.006 g, 0.021 mmol), while the reaction mixture was stirred at 70 °C for 40 min. After that, the solution (pH 2.7) was divided into four vials and left for evaporation at room temperature. Needlelike crystals of KL-3 started to form after 1 week. The crystals were collected by filtration and dried in air. Yield: 0.021 g. IR (KBr pellets, cm\(^{-1}\)) = 3440 (s, br), 1629 (s), 1497 (w), 1416 (w), 1326 (w), 1294 (w), 1135 (m), 1083 (m), 1022 (m), 937 (s), 816 (s), 677 (s), 464 (s). Raman (solid sample, cm\(^{-1}\)) = 969 (s), 890 (m), 801 (w), 695 (m), 633 (m), 570 (m), 320 (w), 207 (m). Single-crystal diffraction data for KLD-1, KLD-2, and KLD-3 were collected on a SuperNova (Agilent Technologies) diffractometer at 120 K with Mo Kα radiation (\( \lambda = 0.71073 \) Å) for KLD-1 and Cu Kα radiation (\( \lambda = 1.54184 \) Å) for KLD-2 and KLD-3. The crystals were mounted in a Hampton cryoloop with Paratone-N oil to prevent water loss. Absorption corrections were applied numerically based on Gaussian integration over a multifaceted crystal model.\(^4\) The SHELXTL software package\(^5\) was used to solve and refine the structures. The structures were solved by direct methods and refined by a full-matrix least-squares method against \( F^2 \) with anisotropic thermal parameters for all heavy atoms (As, K, P, and W) with application of ISOR instructions for the restrained treatment of some heavily disordered K cations. The \( K^+ \) counterions in the structure of KLD-2 with the site occupancy factor less than 0.25 were refined in isotropic approximation. The relative site occupancy factors for the disordered positions of the \( K^+ \) cations as well as O atoms of the crystal water molecules were refined in an isotropic approximation with \( U_{eq} = 0.05 \), then fixed at the obtained values, and refined without thermal parameter restrictions. No Li\(^+\) positions and H atoms of the crystal water molecules were located. H atoms of the phenyl rings of the PhAsO\(_2\)^− and p-arsanilate groups and the amino and methyl groups of polyaniline chains and the located dimethylammonium cations, respectively, were placed in geometrically calculated positions. Because of severe disorder, only 4 DMA\(^+\) cations could be located in the structure of KLD-1 and no DMA\(^+\) cations in the structure of KLD-2, while 7 and 3.5 DMA\(^+\) counterions are present in these structures, respectively, based on elemental analysis. Because of this disorder, there are only 15 highly disordered water molecules in KLD-1 (with O site occupancy from 0.0625 to 0.5) out of 130, the number determined from elemental analysis and TGA for this compound. Similarly, the O positions for only 18.5 out of 92 water molecules were located in the structure of KLD-2. This is consistent with the large solvent-accessible volume remaining in the structures. For the overall consistency, the final formulas in the crystallographic data correspond to the compositions of the bulk materials determined by elemental analysis and TGA. The rather high values of \( R_p \) for KLD-1, KLD-2, and KLD-3...
The other hand, it reduces pH solubility of the organoarsonic acids in a 1 M LiCl medium. On arsonate solution. On the one hand, this slightly improves the (pH 3.0) at 60°C. The aromatic rings of the phenyl (C6H5) and (H2N)C6H4 (or p-aminophenyl) – As = 1.68(3) Å in (H2N)C6H4 (or p-aminophenyl) – As = 1.68(3) Å in 1.671(19)–1.73(2) Å in 2. The tetragonal AsV coordination sphere is completed by a terminal oxo ligand [As–O = 1.68(3) Å in 1 and 1.63(2)–1.68(3) Å in 2] and a C atom of the phenyl (1) or p-aminophenyl (2) group [As–C = 1.89(1) Å in 1 and 1.88(2)–1.90(17) Å in 2]. The aromatic rings are directed outward from the inner cavity of the polyanion, minimizing potential steric hindrances (Figures 1 and S1). The AsV ions of the [RAsVO] groups in S1). The AsV ions of the [RAsVO] groups in 2,486/−2,824 3.308/−2.972.

3. RESULTS AND DISCUSSION

3.1. Syntheses and Crystal Structures. Polyanions 1 and 2 have been prepared by heating of KL-[P8W66] with phenylarsonic (1) or p-arsanlic (2) acid in a 1 M LiCl solution (pH 3.0) at 60°C. The pH of the reaction mixture was adjusted by the addition of glacial acetic acid to the initial organoarsonate solution. On the one hand, this slightly improves the solubility of the organoaarsenic acids in a 1 M LiCl medium. On the other hand, it reduces pH fluctuations while mixing the [P8W66O46]4– and organoaarsenic ligand solutions compared to directly mixing the reagents in 1 M aqueous LiCl followed by the addition of acetic acid to the final mixture. 1 and 2 crystallize as the hydrated mixed potassium/lithium/dimethylammonium (DMA+) salts [K3Li7][{(CH3)2NH}2][{(CH3AsO)4·P8W66O46}13]·H2O (KLD-1) and [K10.5Li14{(CH3)2NH}3.5·[(H2NC6H4AsO)3P8W66O46]·92H2O (KLD-2) in the tetragonal f4 and triclinic P1 space groups, respectively. The precise numbers of K+, Li+, and DMA+ cations as well as crystal water molecules in KLD-1 and KLD-2 were established from elemental and thermogravimetric analyses. 1 and 2 can also be crystallized with Rb+ and Cs+ counterions instead of DMA+; however, 1 and 2 cannot be isolated directly from the reaction mixture without additional counterions.

Single-crystal X-ray diffraction reveals that the structures of 1 and 2 comprise four [RAsV]4– units [R = C6H5 (1) and p-(H2N)C6H4 (2)] that are covalently bound to the two inner rims of the {P8W66} wheel through As–O–W bonds (Figures 1 and S1). The AsV ions of the [RAsV]4– groups in the inner cavity of the polyanion, minimizing potential steric hindrances (Figures 1 and S1). The bond lengths and angles within the {P8W66} framework and organic moieties are in the usual ranges (see Table S2). Two AsV ions occupy opposite (alternating) coordination sites on one rim of the POT wheel, while the other two are located on the other rim, binding to opposite vacant sites, which are in orthogonal positions to the first two (Figure 1b, right),

Table 1. Crystallographic Data and Structure Refinement Details for KLD-1, KLD-2, and KL-3

| sample | KLD-1 | KLD-2 | KL-3 |
|--------|-------|-------|------|
| radiation source | Cu Kα | Cu Kα | Cu Kα |
| empirical formula | C20H20AsK13Li17N10O18P8W66 | C18H20AsK13Li17N10O18P8W66 | C19H20AsK13Li17N10O18P8W66 |
| fw, g mol⁻¹ | 15784.16 | 15079.26 | 14783.50 |
| cryst syst | tetragonal | triclinic | triclinic |
| space group | P4 | P1 | P1 |
| a, Å | 25.194(1) | 24.312(4) | 21.771(7) |
| b, Å | 25.194(1) | 29.978(8) | 24.591(6) |
| c, Å | 25.692(4) | 80.834(2) | 78.910(3) |
| α, deg | 90 | 82.616(2) | 82.697(3) |
| β, deg | 90 | 82.616(2) | 82.697(3) |
| γ, deg | 90 | 82.616(2) | 82.697(3) |
| volume, Å³ | 16308.3(2) | 15049.4(7) | 7073.8(4) |
| Z | 2 | 2 | 1 |
| Dcalc, g cm⁻³ | 3.214 | 3.350 | 3.470 |
| abs coeff, mm⁻¹ | 17.519 | 36.373 | 38.142 |
| F(000) | 14328 | 13528 | 6602 |
| cryst size, mm³ | 0.28 × 0.29 × 0.32 | 0.06 × 0.08 × 0.24 | 0.06 × 0.09 × 0.33 |
| θ range for data collection | 4.10–25.67 | 8.88–66.59 | 8.95–65.09 |
| completeness to θmax, % | 99.5 | 99.5 | 99.3 |
| index ranges | −30 < h < +30, −30 < k < +30, −31 < l < +31 | −27 < h < +27, −28 < k < +28, −35 < l < +28 | −16 < h < +16, −24 < k < +25, −28 < l < +28 |
| refns collected | 153179 | 262401 | 94589 |
| indep refns | 15399 | 52558 | 23947 |
| Rint | 0.1239 | 0.1341 | 0.1351 |
| obsd [I > 2σ(I)] | 13962 | 32564 | 15078 |
| abs corr | numerical based on Gaussian integration over a multifaceted crystal model | 13962 | 32564 | 15078 |
| Tmax/Tmin | 0.0118/0.0844 | 0.0130/0.2352 | 0.0120/0.2044 |
| no. of | 15399/32/469 | 52558/48/1716 | 23947/0/869 |
| GOF on F² | 0.104 | 1.035 | 1.031 |
| Rwp | 0.0487, 0.1280 | 0.0921, 0.2304 | 0.0842, 0.2142 |
| Rw | 0.0562, 0.1360 | 0.1457, 0.2771 | 0.1339, 0.2628 |
| largest diff peak/hole, e Å⁻³ | 2.486/−2.824 | 4.387/−2.824 | 3.308/−2.972 |
resulting in approximately \( C_{2v} \) symmetry (if slight rotations of the phenyl and \( p \)-aminophenyl groups are not considered).

Relatively short As–O bonds compared to the M–O bonds in the complexes of \( \{P_{8}W_{48}\} \) with heterometals (1.9–2.3 Å) cause slight distortions within the \( \{P_{8}W_{48}\} \) skeleton. Thus, the macrocyclic wheel is somewhat tilted toward two \( \{RAsVO\} \) units (Figure 1b, right): the O···O distance between the two O ions coordinated to one AsV constitutes 2.65 Å for 1 and is in the range from 2.63 to 2.68 Å for 2, while the O···O distance between the corresponding O centers of the noncoordinated vacant sites is 3.39 Å for 1 and 3.21–3.36 Å for 2. This distortion probably limits the number of incorporated \( \{RAsVO\} \) groups to four (vs eight), even if larger L/POT ratios are used in the reaction mixture (e.g., 20:1 instead of 10:1), and is responsible for the geometry of the complexes because coordination of the \( \{RAsVO\} \) groups at the four specific positions allows minimization of the strain within the POT skeleton. Charge neutrality for \( KLD-2 \) requires the presence of four protons. The bond-valence-sum calculations\(^{11}\) indicate that these protons are not likely associated with any of the O atoms of the polyanion (see Table S3 for details). At the same time, the relatively low pH used in the synthesis of 2 suggests protonation of the amino groups of the \( p \)-arsanilate ligands, similar to the situation observed for the \( p \)-arsanilate-functionalized polyoxomolybdates.\(^4k\)

3.2. Solution Studies. The solution behaviors of 1 and 2 in aqueous media have been examined by \(^1\)H and \(^{31}\)P NMR spectroscopy. The \(^1\)H NMR spectrum of a \( KLD-1 \) solution in \( D_{2}O \) (Figure S7) exhibits that expected for the phenyl ring combination of a doublet (7.72 ppm) and two triplets (7.61 and 7.54 ppm) in an approximate 2:1:2 integral ratio. The \(^1\)H NMR spectrum of a \( D_{2}O \) solution of \( KLD-2 \) (Figure S8) shows two doublets (7.565 and 6.97 ppm) corresponding to the two pairs of symmetrically equivalent protons of the phenyl rings of the \( p \)-arsanilate ligands, while the signal of the \( NH_{2} \) group overlaps with the strong H\(_2\)O signal. The signals in the spectra of 1 and 2 are significantly shifted compared to those of noncoordinated phenylarsonate [7.765 (d), 7.70 (t), and 7.60 (t) ppm] and \( p \)-arsanilate [7.565 (d) and 6.97 (d) ppm] anions (Figures S7 and S8), indicating the stability of 1 and 2 in an aqueous medium over the short time period of the \(^1\)H NMR measurement.

The solution stability over longer time periods (1 h to 1 day) has been studied using \(^{31}\)P NMR spectroscopy. On the basis of the crystal structures of \( KLD-1 \) and \( KLD-2 \), we expect only a singlet for both polyanions in case they are intact in solution. In addition, two overlapping signals at −6.9 and −7.1 ppm as well as a wider signal contribution downfield to these signals were observed in the solid-state \(^{31}\)P MAS NMR spectrum for \( KLD-1 \) (at a rotation frequency of 15 kHz; Figure S9). The appearance of several signals is most likely due to disorder of K\(^+\) cations bound in the inner cavity of the polyanion to phosphate O atoms that in the crystal lattice renders phosphates bound and not bound to K\(^+\) nonequivalent. Solution \(^{31}\)P NMR spectra were measured at room temperature in several media of various basicity and ionic strength, such as H\(_2\)O (Figures S10 and S11), 1 M LiCl\(_{eq}\) (Figures S12 and S13), 4 M LiCl\(_{eq}\) (Figures S14 and S15), 2 M LiSO\(_4\)/H\(_2\)SO\(_4\) buffer (pH 3.0; Figures S16 and S17), 0.5 M LiOAc (pH 6.76, Figures S18 and S19), and 2 M LiOAc (pH 7.6; Figures S20 and S21) solutions as well as 0.5
M Tris buffer with pH 7.6 (Figures S22 and S23). While the compounds were well-soluble in water, heating has to be applied to dissolve KLD-1 and KLD-2 in Li-based media and in Tris buffer. Already 1 h after redissolution, the spectra of 1 and 2 in H2O and all Li-based media exhibit two sets of closely spaced signals: one at around −6.5/−7 ppm, and the other one slightly shifted upfield, while the exact positions, number, and relative intensities of these signals are changed after 1 day. These results are evident of at least partial decomposition of the polyanions, which most likely occurs by dissociation of the organoarsonate ligands. The cleanest spectra in these media and, in turn, best stability against hydrolysis were observed in 4 M LiCl solutions after 1 h, which exhibit main signals at 7.2 ppm (for 1) and −7.1 ppm (for 2), along with small upfield peaks at −7.6 ppm (1) and −7.3 ppm (2) (Figures S14 and S15), which compare well with the chemical shifts in the solid state and differ from the chemical shift for the P atoms of the noncoordinated {P8W48} wheels in this medium (−6.9 ppm). However, after 1 day, the spectrum of the same solution shows several overlapping signals, similar to the results obtained in the other tested media.

At the same time, the spectra of KLD-1 and KLD-2 solutions in 0.5 M Tris buffer (pH 7.6) exhibit a singlet at −8.3 and −8.4 ppm, respectively, after 1 h, 4 h, and 1 day. The chemical shifts unambiguously differ from the signal at −8.0 ppm observed for non-functionalized {P8W48} in the same medium appearing along with additional small peaks, which strongly supports at least one-day stability of the organoarsonate {P8W48} derivatives 1 and 2 in this medium. Thus, the above results point to a significant potential of 1 and 2 to act as novel organically functionalized POM precursors in Tris aqueous solutions at pH 7–8.

3.3. Recrystallization and Complexation with Heterometal Experiments. For further insight into the hydrolysis processes in the LiCl media, we analyzed crystals isolated from the solution of KLD-2 in 4 M LiCl. Structural analysis revealed the composition K7.2Li23−x[(H3NC6H4AsO)3P8W48O184H2{WO2(H2O)2}0.4].nH2O (KL-3). The three As5+ centers in the polyanion 3 bind to O atoms of the vacant sites situated on opposite rims of the {P8W48} wheel (Figure 2). The two inversion-symmetric As5+ positions are fully occupied, while the remaining As3+ ion (along with its p-aminophenyl and terminal oxo ligands) is disordered over the two remaining positions with equal occupancy. This means that either (a) only a single [(H3NC6H4AsO)3P8W48−O184H2{WO2(H2O)2}0.4]−polyanion type makes up the crystals of KL-3 (with three monoprotonated p-arsanilate ligands bound to the {P8W48} macrocycle) or (b) there is an equimolar mixture of species with two and four organoarsonates, [(H3NC6H4AsO)3P8W48−O184H2{WO2(H2O)2}0.4]−(33.2−x)− and [(H3NC6H4AsO)3P8W48−O184H2{WO2(H2O)2}0.4]−(27.2−x)−, respectively. The additional four vacant sites of {P8W48} in 3 are surprisingly occupied by WVI centers (with a relative site occupancy factor of 0.1), which is related to minor {P8W48} decomposition during heating. This result shows that the {RAs5O} groups in 1 and 2 readily dissociate in slightly acidic aqueous solutions, followed by their recomplexation with {P8W48} POT, indicating complex equilibria in aqueous solutions of KLD-1 and KLD-2, which explains their very complex 31P NMR spectra. This behavior is also similar to that observed previously for SnII complexes of {P8W48}n (K[Sn(O2CC6H4)3]2P8W48O184), K7.5Sn3(Cl2)6P8W48O184 [27].

Interestingly, the coordination mode of As5+ centers in 3 does not allow for a significant bending-type distortion of the POT wheel, as observed in 1 and 2 (Figure 2, right). On the other hand, this results in significant distortion of the arsonate groups, as reflected by the much wider As−O bond length range in KL-3 [As−Oterminal = 1.55(2)−1.83(3) Å; As−Oterminal = 1.69(3) and 1.91(4) Å] compared to KLD-1 and KLD-2. Another consequence is “compression” of the macrocycle toward p-arsanilate groups. Thus, distances between O atoms bound by As5+ centers constitute 2.74−2.75 Å, while the O···O separation of the remaining four vacant sites is 3.64−3.65 Å. The “compression”-type distortion of {P8W48} is not
unprecedented and is commonly observed in its heterometal complexes, which do not possess C4 symmetry.12

To test the ability of using polyanions 2 as precursors for magnetic organoarsenate-functionalized \{P₈W₄₈\} derivatives, we added various heterometals in solutions of KLD-2 in an aqueous 4 M LiCl medium. The microcrystalline product KL-4 isolated from the reactions with FeIII exhibit \{Fe₈(H₃NC₆H₄AsO)₆P₈W₄₈\} stoichiometry based on elemental analysis results. Unfortunately, the small crystal dimensions thus far have precluded single-crystal XRD measurements; however, the IR spectrum for KL-4 (Figure S3) strongly supports coordination of the FeIII ions to the p-arsanilate-functionalized polyanion (see the Supporting Information for details). This implies that KLD-1 and KLD-2 can act as possible novel POM precursors for organofunctionalized heterometal \{P₈W₄₈\} derivatives.

4. CONCLUSIONS

In summary, we have successfully isolated the first examples of the main-group, nonmetal-element-decorated \{P₈W₄₈\} derivatives with the general formula \{[(RAsO)₆P₈W₄₈(OH)₆]Ã³− \[R = \text{C₆H₄ or } p-\text{(H₃N)}C₆H₄\], also representing the first heteropolyoxotungstates functionalized with organoarsenates. In these species, four \{RAsO\} moieties are connected to the POT wheel via As−O−W bonds, resulting in C₃-symmetric complexes. Because of the relatively short As−O bond length compared to the M−O bonds of transition or rare-earth and SnII metal ions, the formation of \{[(RAsO)₆P₈W₄₈(OH)₆]Ã³− \} leads to thus-far-unprecedented distortions of the \{P₈W₄₈\} wheel, which is slightly flexed toward coordinated \{RAsO\} groups in 1 and 2. Our solution studies revealed dissociation of the organoarsenate fragments from the title polyanions in a slightly acidic aqueous medium followed by their rearrangement within the inner POT cavity. Polyoxomolybdates of the composition \{[(H₂NC₆H₄AsO)₆P₈W₄₈(OH)₆H₂O₂(W₃O₁₀)₂O(H₂O)]Ã³− \} have been crystallized as the hydrated mixed K+/Li+ salt as the product of these structural rearrangements. At the same time, the title polyanions appear to be stable in the time frame from 1 h to at least 1 day (depending on the medium) in slightly basic solvents (pH 7.6).

The presence of vacant sites that remain noncoordinated by AsV centers in the inner cavity of the \{P₈W₄₈\} macrocycle in 1–3 and their feasible steric accessibility open perspectives for subsequent functionalization of the organoarsenate–POM hybrids by magnetic metal centers, an avenue that we are currently investigating.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01928.

Experimental details, bond length and bond-valence-sum values, and IR, Raman, and 31P NMR spectra (PDF)

Accession Codes

CCDC 1548225–1548227 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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