Direct Single- and Double-Side Triol-Functionalization of the Mixed Type Anderson Polyoxotungstate \([\text{Cr(OH)}_3\text{W}_6\text{O}_{21}]^{6-}\)

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**Supporting Information**

**ABSTRACT:** Since the first successful triol-functionalization of the Anderson polyoxometalates, the six protons of their central octahedron \(X(OH)_6\) (\(X\) — heteroatom, p- or d-element) have been considered as a prerequisite for their functionalization with tripodal alcohols, and therefore, the functionalization of Anderson structures from the unprotonated sides have never been reported. Here, we describe the triol-functionalization of \([\text{Cr(OH)}_3\text{W}_6\text{O}_{21}]^{6-}\) leading to the single-side grafted anions \([\text{Cr(OCH}_3\text{CH}_2\text{CH}_3}\text{W}_6\text{O}_{21}]^{6-}\) (\(\text{CrW}_6\text{tris-}R\), \(R = -\text{C}_3\text{H}_7, -\text{NH}_2, -\text{CH}_2\text{OH}\)) and the unprecedented double-side functionalized anion \([\text{Cr((OCH}_3\text{CH}_2\text{CH}_3)}_3\text{W}_6\text{O}_{21}]^{-}\) (\(\text{CrW}_6\text{-(tris-C}_2\text{H}_5\text{)}_2\)), despite the lack of protons in the parent anion in the solid state. \(\text{CrW}_6\text{-(tris-C}_2\text{H}_5\text{)}_2\) demonstrates the first example of double-side functionalized Anderson POT with the partially one-side protonated corresponding parent anion. The new heteropolytungstates were characterized by single-crystal X-ray diffraction, elemental analysis, Fourier-transform infrared spectroscopy, thermal gravimetric analysis, cyclic voltammetry, and electrospray ionization mass spectrometry. Density functional theory calculations were performed to investigate and compare the stability among the different isomers of the parent anion \([\text{Cr(OH)}_3\text{W}_6\text{O}_{21}]^{6-}\).

**INTRODUCTION**

Anderson polyoxometalates (POMs) are a class of transformable discrete polynuclear metal-oxo clusters, which contain six edge-sharing pseudo-octahedrally coordinated \(\text{MO}_6\) units (\(M = \text{Mo or W}\)) surrounding a central heteroatom \((X)\) (p- or d-element).\(^5\) The polyoxomolybdate (POMo) \(\text{XMo}_6\) system incorporates a greater variety of heteroatoms than the respective polyoxotungstate (POT) \(\text{XW}_6\) system, despite both being structurally identical. The physical and chemical properties of Anderson POMos and POTs are highly versatile and depend on the kind of the heteroatom, counterion, and its organic functionalization. The Anderson POMs are divided into two types according to the protonation state of the six triple-bridged oxygen atoms, \(\mu_3\)-O, connecting the heteroatom with the addenda atoms (Mo and W, respectively). The general formula of the non-protonated A-type is \([\text{X}^n\text{Me}_6\text{O}_{24}]^{(12-n)^-}\) with the heteroatom exhibiting its highest oxidation state (e.g., \(\text{I}^3, \text{Sb}^5, \text{Te}^{65}\)), whereas the fully protonated B-type has the general formula \([\text{X}^{n+}(\text{OH})_6\text{Me}_6\text{O}_{19}]^{(6-n)^-}\) with the heteroatom exhibiting lower oxidation states (e.g., \(\text{Ni}^{2+}, \text{Co}^{2+}, \text{Fe}^{3+}, \text{Al}^{10+}\)).\(^1\) For a long time, the partial protonation (number of protons less than 6) of B-type Anderson POMos and POTs was known only for \(\text{Pt}^\text{IV}\)-centered anions, which usually do not possess an integer number of protons and tend to form dimeric structures via hydrogen bonds.\(^10\) Recently, the mixed type anion \([\text{Cr(OH)}_3\text{W}_6\text{O}_{21}]^{6-}\) was reported by Kortz\(^11\) and our group,\(^12\) however, the existence of a heteropolyanion with a molar ratio \(\text{Cr}/\text{W} = 1.6\) was predicted back in the 1970s.\(^13\) X-ray analysis and bond valence sum calculations showed that in solid-state \([\text{Cr(OH)}_3\text{W}_6\text{O}_{21}]^{6-}\) contains an unprotonated “A-side” and a protonated “B-side” (three protonated \(\mu_3\)-O atoms).\(^11\) Using an alternative synthetic procedure with a different component ratio (see the Supporting Information), \(\text{Na}_6[\text{Cr(OH)}_3\text{W}_6\text{O}_{21}]\) has been obtained with the same protonation state (Tables S10 and S11).

Among the various synthetic strategies for the organic functionalization of POMs,\(^14\) alkoxylation has gained much attention because of the diversity and tunability of alkoxyl ligands, especially when using the disk-shaped Anderson type anions with a wide spectrum of central heteroatoms.\(^15\) The resulting hybrid materials showed interesting application in the synthesis of bioinorganic hybrid materials,\(^16\) supramolecular self-assembly,\(^16c\) charge storage,\(^16d\) metal–organic frameworks,\(^16e\) nanostructured materials,\(^16f\) and photochemistry.\(^16g\) Since the first tris-alkoxo functionalized \([\text{RC(CH}_2\text{OH)}_3\text{R} = -\text{NH}_2, -\text{OH}, -\text{CH}_2\text{OH}, \text{etc.}]\) Anderson-type hybrid
POMs were published,\textsuperscript{17} there was a clear conviction that only B-type (protonated) POMs can be tris-functionalized as the incorporation of tris-ligands represents a nominal dehydrative condensation reaction,\textsuperscript{17} where the protons of the POM’s hydroxo groups are putatively replaced by carbon atoms of the organic ligand. Moreover, even in the case of the formation of a \( \chi \) Anderson isomer, in which the ligand is anchored on two \( \mu_2 \)-O atoms and one \( \mu_3 \)-O atom, the addition of a stoichiometric amount of protons for the protonation of the \( \mu_2 \)-O atom was considered necessary.\textsuperscript{18} In contrast to the B-type clusters, tris-functionalized A-type anions have never been reported, but when the \([\text{MoO}_3\text{O}_{24}]^{5-}\) POM is refluxed under acidic conditions, it becomes protonated and can be methylation, yielding the methoxyl-derivative \([\text{MoO}_3\text{O}_{24}(\mu_2\text{OMe})]^{14-}\).\textsuperscript{19} Interestingly, the protonation in \([\text{MoO}_3\text{O}_{24}]^{5-}\) occurs rather at the \( \mu_3 \)-O atoms than at the \( \mu_2 \)-O sites, despite the former being usually less basic. The potential reactivity of the unprotonated \( \mu_2 \)-O atoms of A-type Anderson POMs to undergo functionalization was shown during the crystallization of aurone synthase from \textit{Coreopsis grandiflora} (\textit{cgAUS1})\textsuperscript{20} using \([\text{TeW}_6\text{O}_{25}]^{8-}\) (TEW) as additive because the POM forms a covalent bond with a glutamic acid via two of its \( \mu_2 \)-O atoms, yielding the first proteinogenically functionalized \([\text{TeW}_6\text{O}_{25}O_2(\text{Glu})]^{7-}\) anion.\textsuperscript{21}

Tris-functionalized Anderson POMs, which make up a lion’s share in alkali metal chemistry of Anderson-type POMs, are mainly synthesized from octamolybdate \([\text{MoO}_3\text{O}_{24}]^{2-}\) in organic solvent or from the parent Anderson anion in aqueous solution under reflux.\textsuperscript{22-25} Interestingly, the role of the protons is considered important for both synthetic routes, but their importance is even emphasized in the latter case, namely, during the self-assembly reaction starting from octamolybdate in the presence of the heterotatom and tris-ligand.\textsuperscript{2} Hydrothermal reaction, which has been proven as an effective method for the preparation of POMs is rarely utilized for alkoxylation but was successfully applied for the tris-modification of the fully protonated B-type POMo \([\text{Cr-(OH)}_3\text{MoO}_3\text{O}_{18}]^{13-}\).\textsuperscript{26} Depending on the stoichiometric ratio between the parent anion and the triol-ligand, both single- and double-side POMos were obtained.\textsuperscript{23}

Attempts to obtain organically functionalized Anderson-type POTs were unsuccessful for a long period because of the inertness of the bridging oxygen atoms in the \{WO\textsubscript{6}\} octahedra. However, in 2016, we demonstrated that the B-type anion \([\text{Ni(OH)}_3\text{WO}_{18}]^{13-}\)\textsuperscript{27} can be covalently modified from one side with pentaerythritol \(\text{CH}_2\text{OH}\) and from the other side with triol-ligands \(\text{CH}_2\text{OH}\), using an acyclic aqueous solution with excess of triol-ligand.\textsuperscript{28} More recently, Li and Wei extended the family of single-sided functionalized Anderson-type POTs by \textit{Al}\textsuperscript{III}, \textit{Cr}\textsuperscript{III}, and \textit{Co}\textsuperscript{III}-containing structures, which were obtained via direct assembly of the preformed heterotatom-tris-ligand complex and ortho- or ditungstate in aqueous solution.\textsuperscript{29} Despite using a fourfold excess of the triol-ligand, the authors claim that the following complexes were formed, which then react with the tungstates. The parent inorganic Anderson structures containing \textit{Al}\textsuperscript{III} and \textit{Co}\textsuperscript{III} are not reported yet; however, the authors made a conclusion based on the functionalization mode that these structures should be three-protonated from one side as the \([\text{Cr(OH)}_3\text{WO}_{21}]^{16-}\) anion. Note, that all four existing functionalized Anderson POTs were decorated from one side by aqueous one-pot reactions.

To investigate the possibility of triol-ligand attachment to the mixed-type anion \([\text{Cr(OH)}_3\text{WO}_{21}]^{16-}\), which in a solid state demonstrates protonated and proton-free sides, we explored hydrothermal synthesis for the alkoxylation of POTs. Herein, we report for the first time the successful double-sided tris-functionalization of an Anderson-type POM, which is not fully protonated in the pure inorganic parent form, yielding \([\text{Cr(OH)}_3\text{CC}(\text{CH}_3)_2\text{WO}_{18}]^{3-}\) (\textit{CrW}_6-\textit{tris-(C}_3\text{H}_7\text{O}_3\text{)}). Furthermore, the proposed controlled hydrothermal synthesis allows the synthesis of the single-side functionalized \([\text{Cr(OH)}_3\text{CC}(\text{CH}_3)_2\text{WO}_{18}]^{3-}\) (\textit{CrW}_6-\textit{tris-(C}_3\text{H}_7\text{O}_3\text{)}) and \([\text{Cr(OH)}_3\text{CC}(\text{CH}_2)\text{OHWO}_{18}]^{3-}\) (\textit{CrW}_6-\textit{tris-(CH}_2\text{OH})). Among the five reported functionalized Anderson POTs \([\text{Ni(OH)}_3\text{WO}_{18}(\text{OCH}_2)_3\text{CCH}_2\text{OH}]^{4-}\), \([\text{Cr(OH)}_3\text{CC}(\text{CH}_3)_2\text{WO}_{18}]^{3-}\) (\textit{CrW}_6-\textit{tris-(C}_3\text{H}_7\text{O}_3\text{)}), \([\text{Cr(OH)}_3\text{CC}(\text{CH}_3)_2\text{WO}_{18}]^{3-}\) (\textit{CrW}_6-\textit{tris-(C}_3\text{H}_7\text{O}_3\text{)}), \([\text{Cr(OH)}_3\text{CC}(\text{CH}_2)\text{OHWO}_{18}]^{3-}\) (\textit{CrW}_6-\textit{tris-(CH}_2\text{OH})), \([\text{Co}(\text{OCH})_3\text{WO}_{18}(\text{OCH}_2)\text{CC}(\text{CH}_2)\text{OH}]^{3-}\). \([\text{CrO}_3\text{WO}_{18}(\text{OCH}_2)\text{CC}(\text{CH}_2)\text{OH}]^{3-}\) (\textit{CrW}_6-\textit{tris-(C}_3\text{H}_7\text{O}_3\text{)}), which represents the first example of a double-side functionalized Anderson POT, which is usually more stable and could therefore be an excellent building block candidate for the design of novel metal oxide-based materials.

## EXPERIMENTAL SECTION

### Physical Methods

Infrared spectra (4000–400 cm\(^{-1}\)) of all samples were recorded on a Bruker Vertex 70 IR Spectrometer equipped with a single-reflection diamond-ATR unit. Elemental analysis was performed with an ICAP 6500 series inductively coupled plasma-optical emission spectrometry (ICP-OES) spectrometer (Thermo Scientific, USA). The ICP-OES was equipped with a standard sample introduction system consisting of a concentric nebulizer and a cyclonic spray chamber. Transportation of sample solutions was performed by the peristaltic pump of the ICAP 6500 coupled to an ASX-520 auto sampler (Cetac, USA). Per element two sensitive and noninterfered emission lines were used, the first line for measurement and the second line for quality control. The water content was determined by thermal gravimetric analysis (TGA) with a Mettler SDTA851e thermogravimetric analyzer under nitrogen flow with a heating rate of 5 K min\(^{-1}\) in the region 298–1023 K. Mass spectrometry (MS) was performed with an electrospray ionization (ESI)-Qq-tofTOF supplied by Bruker Daltonics Ltd. Bruker Daltonics Data Analysis software was used to analyze the results. The measurement was carried out in a 1:1 mixture of water/McCN, collected in negative ion mode and with the spectrometer calibrated with the standard tune-mix to give an accuracy of ca. 5 ppm in the region of \(m/e\) 300–3000. The cyclic voltammetry measurements were carried out using a HEKA PG 390 potentiostat at room temperature. A conventional three-electrode glass cell of 3 mL capacity was used. A 2 mm diameter glassy carbon disk electrode was used as working electrode (GCE). A platinum wire served as the counter electrode and a normal hydrogen electrode served as the reference electrode. All solutions were deoxygenated using argon gas for 10–15 min prior to electrochemical experiments. X-ray powder diffraction was performed on a Bruker D8 ADVANCE diffractometer, Cu \(\text{K}\alpha\) radiation, \(\lambda = 1.54056\) Å, LYNXEYE silicon strip detector and SolX energy dispersive detector, variable slit aperture with 12 mm, 8\(^\circ\) \(\leq \theta \leq 20\) \(^\circ\).

### X-ray Diffraction on Single Crystals

The X-ray data were measured on a Bruker D8 VENTURE equipped with a multilayer monochromator, Mo \(\text{K}\alpha\) Incoatec Microfocus sealed tube, and Kryoflex cooling device. The structure was solved by direct methods and refined by full-matrix least-squares. Nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were inserted at calculated positions and refined with riding coordinates. The following software was used for the structure-solving procedure: frame integration, Bruker SAINT software package, using a narrow-frame algorithm (absorption correction), SADABS (structure solution), SHELXS-2013 (refinement), and SHELXL-2013 (refinement),
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SHEXL-2013,27 OLEX2,28 and SHELXL29 (molecular diagrams). Experimental data and CCDC-codes can be found in Table S10.

**Computational Methods.** All density functional theory (DFT) calculations were carried out using Gaussian (G16 rev. B01).23 The geometries and vibrational modes of all molecules were computed using unrestricted DFT using the hybrid exchange–correlation functionals PBE0,123 the def2-TZVP14 basis set, and implicit aqueous solvation through application of the polarizable continuum model.34 As this level of theory has been demonstrated to work well in predicting bond distances, nuclear magnetic resonance shifts, and relative protonation energies,35,36 an ultrafine integration grid with extra-tight convergence criteria was used in all computations. In addition, DFT calculations for the three isomers of [Cr(OH)3W6O21]6− were performed using PBE37 and B3LYP38,39 as exchange–correlation functionals to gauge the influence of the functional, and the relative enthalpies divide the three different methodologies differ by less than 1 kcal/mol (see Table S13). For all Cr(III) species, a multiplicity of 4 was assumed. Spinc contamination was found to be less than 10% for all species. Energies and optimized geometries are provided as the Supporting Information.

**Syntheses.** All materials were purchased from Sigma-Aldrich and used without further purification.

**Synthesis of Na3[Cr((OCH2)3CC2H5)2W6O18]-17H2O (Na3CrW6-tris-C2H5).** Na3WO4·2H2O (6.6 g, 20 mmol) was dissolved in 80 mL of water before adding 20 mL of HCl (1.0 M). Cr(NO3)3·9H2O (1.33 g, 3.3 mmol) was dissolved in water (10 mL) and added dropwise to the acidified solution of Na3WO4·2H2O. The molar ratio of Cr5+·WO42−·H+/H2O in the aqueous solution was 1:6:6 (Cr/W/H+). The reaction mixture was kept for 3 days under ambient conditions to achieve crystallization. Colorless crystals of Na3[Cr((OCH2)3CC2H5)2W6O18]-17H2O (CCDC 1842741), Na4(C4H12N)2·Na3[CrW4O15]2·N2H4·5H2O (CCDC 1842742), and Na5CrW6·17H2O (CCDC 1842739) were obtained in 61%, 60%, and 66% yields, respectively. Elemental analysis found (calculated) for Na4(C4H12N)2·Na3[CrW4O15]2·N2H4·5H2O: Na 5.26 (7.00); Cr, 2.36 (2.46); W 51.28 (50.98). IR (see Figure S1 in the Supporting Information): 3322 (b), 3025 (w), 2873 (w), 1613 (m), 1120 (m), 1072 (w), 932 (s), 707 (s), 609 (s), 505 (s), 439 (s) cm−1.

**Synthesis of Na5[Cr((OCH2)3CC2H5)W6O18]-17H2O (Na5CrW6-tris-C2H5).** The synthesis of Na5[Cr((OCH2)3CC2H5)W6O18]-17H2O was similar to that of Na3CrW6-tris-C2H5, with the exception that the reaction mixture was heated at 140 °C for 48 h. The blue-green crystals appeared in 1 week after the addition of KCl solution (1.0 M). Elemental analysis found (calculated) for Na5CrW6·17H2O: Na 5.29 (5.18); K, 2.46 (2.46); W 51.30 (51.06). IR (see Figure S1 in the Supporting Information): 3322 (b), 3025 (w), 2873 (w), 1613 (m), 1120 (m), 1072 (w), 932 (s), 707 (s), 609 (s), 505 (s), 439 (s) cm−1.

**Synthesis of Na3K3[Cr((OCH2)3CC2H5)2W6O18]-13H2O (Na3K3CrW6-C2H5).** The synthesis of Na3K3[Cr((OCH2)3CC2H5)2W6O18]-13H2O was similar to that of Na3CrW6-tris-C2H5. The synthesis of Na5K3[Cr((OCH2)3CC2H5)2W6O18]-17H2O was similar to that of Na3K3CrW6-tris-C2H5 with the exception that the pentanethiol (tris-CH2OH) was used instead of 1,1,1-tris(hydroxymethyl)propane. After the reaction, tetramethylammonium chloride (0.3 g, 2.5 mmol) was added to induce crystallization. Colorless crystals of Na3K3[Cr((OCH2)3CC2H5)2W6O18]-13H2O (CCDC 1842739) were obtained in 67% yield. Elemental analysis found (calculated) for Na3K3CrW6·13H2O: Na 3.42 (3.45); Cr 2.44 (2.44); W 55.30 (54.98). IR (see Figure S11 in the Supporting Information): 3322 (b), 3025 (w), 2873 (w), 1613 (m), 1120 (m), 1072 (w), 932 (s), 707 (s), 609 (s), 505 (s), 439 (s) cm−1.

**RESULTS AND DISCUSSION**

**Synthesis and Structures.** Initially, an aqueous solution of Cr3+·WO42− (C = 0.2 M)− H+ was prepared at a molar ratio of 1:6:6 (Cr/W/H+) and a final pH of 5.7. The reaction mixture was kept for 3 days under ambient conditions to achieve equilibrium in the solution. Because the initial solution (molar ratio of Cr3+·WO42−·H+) had a lower pH compared with the values reported for the synthesis of the parent anion [Cr(OH)3W6O21]6− (pH ≈ 8),11,12 ESI-MS was used to aid elucidation of the speciation in solution. The ESI-MS spectra (see Figure S11, Table S8, Supporting Information) of the solution with Cr3+·WO42−·H+ measured after 1, 3, and 10 days at pH 5.7 are the same and are dominated by peaks which can be assigned to isopolynitratefragments ([WmO1uw]2−, w = m−1) on Na3W6O212− or Na3W6O212−, where w = 1−6. Decomposition fragments of [Cr(OH)3W6O212−] (e.g., [Cr2W4O11]−, [Cr3W3O11]−, [Cr4W2O15]−, [Cr5W2O18]−, [Cr6W2O20]−, and Na3W6O212−) were also present in the spectra. It should be noted that the relatively low pH of the initial solution does not lead to the formation of the elusive fully protonated B-type hexatungstochromate, and none of the spectra contains signals at m/z = 515.19, 773.29, or 784.27, where the fully protonated species [Cr(OH)4W6O18]4−, [H2Cr(OH)W5O17]4−, and Na3[Cr(OH)6W6O18]2− would have occurred.

A threefold excess of the tris-ligand was added to 20 mL of the respective stock solution prior to the hydrothermal reaction. The single-side functionalization of the [Cr(OH)3W6O21]6− is possible under hydrothermal conditions at a synthesis temperature of 140 °C leading to the formation of CrW6-tris-R (R = C2H5−, NH2−, CH2OH). At 150 °C, the crystallization of a mixture of single- and double-side decorated anions is observed, whereas at 160 °C, the crystallization of solely the double-functionalized product CrW6-tris-(tris-C2H5)2 occurs (Scheme 1). A further increase in the synthesis temperature leads to the decomposition of the ligand. This synthetic route indicates that the temperature is the key factor in the formation of the double-side product. All hybrid PTOs were crystallized as their alkali salts, namely, Na5CrW6-tris-(tris-C2H5)2·13H2O (CCDC 1842741), Na5CrW6-tris-(tris-C2H5)2·17H2O (CCDC 1842742), Na5CrW6-tris-NH2·17H2O (CCDC 1842739), and Na5CrW6-tris-(tris-CH2OH)·19H2O (CCDC 1842740). The successful double-sided functionalization can be followed visually by the color of the crystals, as single-side alkoxo-decorated compounds are of pine green color, while the double-side decorated Na5CrW6-tris-(tris-C2H5)2·13H2O exhibits a pink color, which is characteristic for anhydrous chromium(III) salts indicating a different Cr3+ coordination sphere compared with CrW6-tris-R.
Scheme 1. Synthesis of CrW6-(tris-C2H5)2 and CrW6-tris-R (R = −C2H5, −CH3OH, −NH2); HT = Hydrothermal Synthesis; Color Code: WO6, Pink Octahedra; Cr, Green; O, Red; C, Black; H, White

Applying the proposed method, [Cr(OH)3W6O21]6− can be asymmetrically functionalized in two steps, where two different organic groups are selectively grafted on each side. The reaction of CrW6-(tris-C2H5) with tris-CH3OH at 160 °C leads to the formation of the asymmetric product CH3OH-tris-C2H5 that was proven with ESI-MS (Figure S9, Table S6). The possibility of the asymmetric step by step functionalization of [Cr(OH)3W6O21]6− proves the crucial role of the synthesis temperature.

Because the introduced organic ligands present active functional groups, Anderson-type hybrids can be utilized as precursors for further post-functionalization via imine, amide, or ester bond formation. The post-functionalization of CrW6-tris-NH2 with cinnamic acid in acetonitrile was performed using a well-established protocol. The successful formation of a new hybrid can be seen in the ESI-MS spectrum of the reaction mixture (Figure S10, Table S7).

Both double-side and single-side decorated compounds show the characteristic Anderson-type structure with six edge-shared WO6 arranged hexagonally around the central CrO6. The Cr−O bond lengths are in the range of 1.947(6)−1.969(5) Å for CrW6-(tris-C2H5)2, 1.964(7)−1.977(8) Å for CrW6-tris-C2H5, 1.956(4)−1.993(4) Å for CrW6-tris-NH2, and 1.960(1)−1.997(9) Å for CrW6-tris-CH3OH, which is in good agreement with the corresponding bond lengths of the parent Anderson-anion [Cr(OH)3W6O21]6−. Structural analysis indicates that the bond lengths of all three types of W−O bonds (W−μ2−O, W−μ−O, and W:=Oterminal) are also close to those of the parent species [Cr(OH)3W6O21]6− and corresponding POT analogues.

Mechanistic Proposal. For real-time observation of the self-assembly of CrW6-(tris-C2H5)2 under hydrothermal condition, aliquots for ESI-MS of the reaction solution were taken after 12, 24, and 48 h from the moment the reaction had begun. The measured spectra for all time intervals contain the same peaks with slightly different intensities, which can be assigned to the target compound CrW6-(tris-C2H5)2 (m/z = 568.6 for triple-charge, m/z = 853.4 and 864.4 for double-charged), the single-side decorated CrW6-tris-C2H5 anions, their decomposition fragments, and isopolyytungstate

fragments with lower nuclearity ([WmO3m+1]2−, H[WmO3m+1]− or Na[WmO3m+1]−, where m = 1−4) (see Figure S12, Table S9, Supporting Information). The absence of signals at m/z = 515.19, 773.29, or 784.27 is assigned to [Cr(OH)fiWmO4+1]2−, H[Cr(OH)fiWmO4+1]2−, and Na[Cr(OH)fiWmO4+1]2−. According to the ESI-MS spectra recorded from the reaction solution, all the Cr-containing anions are coordinated to triol-ligand, pointing toward the alkylation mechanism proposed by Li and Wei for single-side functionalized structures, according to which free Crfi ions and ligand molecules first formed the complex (Cr(OCH3)2Crfi) before further reacting to the functionalized anion (Scheme 2A).

DFT calculations were carried out to determine the most likely protonation sites and proton distribution of [CrW6O24]9− (CrW6) in aqueous solution. The non-protonated anion CrW6 was optimized, and the most nucleophilic O atoms according to their molecular electrostatic potential were found to be the μ2−O atoms (see Figure S14). Moreover, the enthalpies of the [Cr(OH)3W6O21]6− isomers were computed for the states when the proton is localized on a triply-bridging oxygen (μ−O), doubly-bridging oxygen (μ2−O), or terminal oxygen (Ot) atom. The relative enthalpies (see Table S12) show that the triply-bridging (μ−O) sites are the most probable ones to be protonated, in agreement with the existing experimental data. To investigate and compare the formation energies of the different protonation states in [Cr(OH)fiWmO24−x]9− (x = 0−6), the different protonation states and isomers of protonation states were optimized by DFT and enthalpies computed through normal mode analysis. The different isomers of each protonation state of [Cr(OH)fiWmO24−x]9− (x = 0−6) were structurally optimized and the relative energies computed as protonation enthalpies (Tables S14−S16). The only isolated11,12 in solid-state isomer [Cr(OH)fiWmO21]5− has three possible different positional isomers, namely, two fac isomers (one with all protons on the same side (fac1) and one with a proton on the opposite side (fac2) of the anion) and one mer isomer (mer)
The relative enthalpies of these isomers are shown in Figure 1 and reveal that the fac1-[Cr(OH)6W6O18]3− (three protonated μ3-O atoms from one side) is lower in energy than the other two isomers by 4 and 8 kcal/mol, respectively, suggesting that at the very least the fac1-isomer is the dominant form of the tri-protonated molecule.

The computed bond distances in the optimized fac1-[Cr(OH)6W6O18]3− structure agree well with those observed experimentally (see Supporting Information Figure S12, Table S10 and CSD 1870211) in square brackets for [Cr(OH)6W6O24]3−, with W=O 1.740−1.752 Å [1.723−1.765 Å], W−μ3-O 1.931−1.951 Å [1.919−1.965 Å], W−μ2-O 2.109−2.399 Å [2.094−2.303 Å], Cr−O 1.967−2.008 Å [1.964−2.003 Å] and W−W 3.194−3.435 Å [3.149−3.375 Å].

Table 1. Enthalpies of Stepwise Protonation of [CrW6O24]3− According to Eq 1a

| reactant | product | ΔH (kcal/mol) |
|----------|---------|---------------|
| [CrW6O24]3− | [Cr(OH)3W6O21]6− | 49.5 |
| [Cr(OH)3W6O21]6− | [Cr(OH)2W6O22]7− | −36.9 |
| [Cr(OH)2W6O22]7− | [Cr(OH)W6O23]8− | −22.8 |
| [Cr(OH)W6O23]8− | [Cr(OH)W6O19]4− | −15.4 |
| [Cr(OH)W6O19]4− | [Cr(OH)W6O18]3− | −7.01 |

*aIn the cases where several protonated isomers exist, only the enthalpy of the most stable isomer of each protonated species is given.

The enthalpy of protonation decreases by 40 kcal/mol when proceeding from the unprotonated to the penta-protonated anion, reflecting at least in part the decreasing charge of the cluster ion. The estimation with sufficient accuracy of the absolute pKₐ’s of the different isomers using computed free energies of protonation is often difficult, even for organic molecules and is not attempted here. It is, however, interesting to note that while the protonation enthalpy changes by ca. +6−7 kcal/mol for each added proton in most cases, the addition of a proton to the tri-protonated species is +14 kcal/mol larger than the addition of a proton to the di-protonated species, which may well give an indication as to why in particular the tri-protonated species is generally observed experimentally.

Mizuno et al.41 proposed a mechanism for the alkoxylation of lacunary Keggin anions [A-α-XW₆O₃₄]₄− (X = Si, Ge) involving the instantaneous protonation of oxygen atoms followed by a dehydrative condensation reaction, which could also be a possible mechanism for the formation of Cr₇W₆(tris-C₃H₅)₂ (Scheme 2B) considering the fact that mono- and di-protonated Cr₇W₆(tris-C₃H₅)₂ were present in the ESI-MS spectra (m/z = 835.3 for Na₄[H(Cr(OCH₂)₃CC₃H₅W₆O₁₈)]²− and 845.8 for Na₃[H(Cr(OCH₂)₃CC₃H₅W₆O₂₁)]²−) (see Figure S12, Table S9, Supporting Information) and that protonation of [Cr(OH)₆W₆O₂₄]³− (x = 0−6) is likely to be exothermic under most conditions according to DFT protonation enthalpies (Table 1). Both suggested mechanisms overcome the putative impossibility of functionalizing A-type Anderson POMs.

**Electrospray Ionization Mass Spectrometry.** Further evidence for the existence of the intact Cr₇W₆(tris-C₃H₅)₂ (Figure 1) and Cr₇W₆-tris-R (R = −C₃H₅ −NH₂ −CH₃OH) (see the Supporting Information) in solution and their exact stoichiometric composition was obtained from ESI-MS. The most intense peak at m/z = 568.6 (calcd m/z = 568.6) in the ESI-MS spectrum of Cr₇W₆-(tris-C₃H₅)₂·13H₂O (Figure 2) corresponds to the triply charged anion [Cr-((OCH₂)₃CC₃H₅)₆W₆O₁₈]³− (Cr₇W₆-tris-C₃H₅)₂). The peaks of the doubly charged H[Cr-((OCH₂)₃CC₃H₅)₆W₆O₁₈]²− and Na[Cr-((OCH₂)₃CC₃H₅)₆W₆O₁₈]²− appeared at m/z = 853.4 (calcd m/z = 853.4) and m/z = 864.4 (calcd m/z = 864.4), respectively. The double-side capping effect enhances the stability of the complex and leads to an almost complete absence of decomposition fragments, which are usually unavoidable in POM MS spectra.42 The ESI-MS spectra of the Cr₇W₆-tris-R structures represent a more complex character exhibiting a peak envelope, which can be unambiguously assigned to the doubly-charged anions Na₃H[Cr₇W₆-tris-R]²− (x = 1−3; see Figures S6−S8, Tables S3−S5, Supporting Information) indicating the presence of the intact one-side grafted clusters in solution. A series of peak envelopes in the
rest of the spectra could be assigned to different common POMs fragments (HWO₄⁻, W₂O₇⁻, Na₂W₂O₇⁻, W₇O₁₆⁻, W₂O₁₀⁻, etc.) and some more specific decomposition products, of which the most intensive are [Cr₆W₃O₁₀(OCH₂)₃CR]²⁻, [Cr₆W₄O₁₃(OCH₂)₂CR]³⁻, and H⁻[Cr₆W₄O₁₀(OCH₂)₂CR]⁻ (Figures S6--S8, Tables S2--S4, Supporting Information).

**Electrochemistry.** The electrochemical behaviors of the single-side functionalized Cr₆W₆-tris-C₂H₅ and double-side functionalized Cr₆W₆-(tris-C₂H₅)₂ have been studied by cyclic voltammetry (Figure S13). For Cr₆W₆-tris-C₂H₅, one irreversible oxidation wave is observed at 0.480 V and attributed to the Cr(VI/III) couple. In the cathodic domain, two successive reductions at −0.259 and −0.455 V have been measured (Figure S13A), corresponding to the reduction of the central Cr ion (Cr(III/II) and Cr(II/0 couples). The cyclic voltammogram of Cr₆W₆-(tris-C₂H₅)₂ does not exhibit either oxidative or reduction processes (Figure S13B). The more concealed position of Cr in the double-side decorated anion most likely affects the absence of redox waves in the case of Cr₆W₆-(tris-C₂H₅)₂. The absence of reduction processes for tungsten in both cases is caused by the fact that Anderson anions represent type II POMs with two terminal oxo ligands per W atom, which lacks a nonbonding orbital for electrons acceptance.

**IR Spectroscopy.** IR spectroscopy was applied to investigate the anion in Na₅Cr₆W₆-(tris-C₂H₅)₂·13H₂O, K₂Na₃Cr₆W₆-tris-C₂H₅·17H₂O, Na₅H₂Cr₆W₆-tris-NH₂·17H₂O, and Na₄(C₂H₅₇N)₃Cr₆W₆-tris-CH₂OH·30H₂O (see Figure S1, Table S1, Supporting Information). The characteristic peaks of the core structure in Cr₆W₆-(tris-C₂H₅)₂ and Cr₆W₆-tris-R (R = −C₆H₄ −NH₂ −CH₂OH) are all in agreement with the peaks observed in the spectrum of Na₅[Cr(OC₃H₅)]₂W₀₂₁·22H₂O. The stretching vibrations of the terminal W=O units appears within the range of 936–932 cm⁻¹. The peaks at approximately 865 cm⁻¹ and in the region of 420–800 cm⁻¹ correspond to the antisymmetric and symmetric deformation vibrations of W−O−W and W−O−Cr bridging frames. The peaks appearing at ~1100 and 1050 cm⁻¹ could be assigned to C−O stretching vibrations, indicating the successful grafting of tri-ligands. The spectrum of Cr₆W₆-(tris-C₂H₅)₂ is slightly different from that of the single-functionalized products, which is associated with their lower symmetry.

**CONCLUSIONS**

In conclusion, for the first time, we organically functionalized the Anderson POT from two sides and showed that the double-side functionalization is possible even in the case when the parent inorganic anion state exhibits only three protons in the solid. It was generally accepted that it is not possible to graft triol ligands onto the Anderson anions, which represent unprotonated μ₃-O atoms in their structures as confirmed by single crystal X-ray analysis. By varying the synthesis temperature, both the double- and single-side tris-modified Cr-centered Anderson POMs have been obtained in good yields (>60%). DFT studies revealed the fac3-[Cr(OH)₃W₀₂₁]⁶⁻-isomer (three protons attached from one side) as the most stable form of all triply protonated isomers, which is therefore likely to dominate over the other two possible isomers (mer and fac3) in solution. This finding supports the fact that only the three-protonated [Cr(OH)₃W₀₂₁]⁶⁻ and the unprotonated [Cr₆W₄O₁₃(OCH₂)₂CR]⁶⁻ Cr₆W₆-tris-R can be isolated in solid state. DFT in itself does not claim to conclusively predict that the degree of protonation is going to be the major one under the synthetic conditions but it provides general insights into possible protonation states of Cr₆W₆ anion. The DFT studies together with the real-time ESI-MS experiments suggest two principal mechanisms of Cr₆W₆-(tris-C₂H₅)₂ formation, which include either potential {triol-Cr³⁺} complexes or protonated H₃Cr₆W₆-tris-C₂H₅ (x = 1−3). The new compound Cr₆W₆-(tris-C₂H₅)₂ can be seen as a "game changer" for alkyloxylaion of A-type Anderson POMs, exhibiting new properties that differ from those of the already existing hybrids based on the protonated Anderson archetype. This can be expected because the physical and chemical properties of Anderson POMs highly depend on the nature of the heteroatom, which for A-type Anderson POMs and POMs are highly charged p- and d-elements. Applying the proposed synthetic way, mixed-type Anderson POMs can be asymmetrically functionalized in two steps, where two different organic groups are selectively grafted on each side. The asymmetric product formation was proven by ESI-MS. In the future, asymmetrically functionalized Anderson derivatives can be introduced into oligomers in a controlled manner by, for example, applying click-chemistry reactions.

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Synthetic details and spectroscopic data along with structural characterizations of the new compounds (PDF)

Computationally optimized structures in cartesian coordinates are supplied as a multi-xyz file (XYZ)

**Accession Codes**

CCDC 1842739–1842742 and 1870211 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**

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