

The first tris-functionalized Anderson-type heteropolytungstate

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Abstract – $\text{Na}_2[\text{TMA}]_2[\text{Ni}(\text{OH})_3\text{W}_6\text{O}_{18}(\text{OCH}_2)_3\text{CCH}_2\text{OH}]$ represents the first covalent tris-functionalized Anderson-type heteropolytungstate and was characterized by single-crystal X-ray diffraction, electro spray ionization mass spectrometry, TGA and IR spectroscopy. Zeta potential measurements in solutions containing human serum albumin were performed to investigate electrostatic interactions with $[\text{Ni}(\text{OH})_3\text{W}_6\text{O}_{18}(\text{OCH}_2)_3\text{CCH}_2\text{OH}]^{4-}$.

Key words – polyoxometallates, hybrid organic-inorganic compounds, Anderson anion, tris-functionalization, crystal structure.

I. Introduction

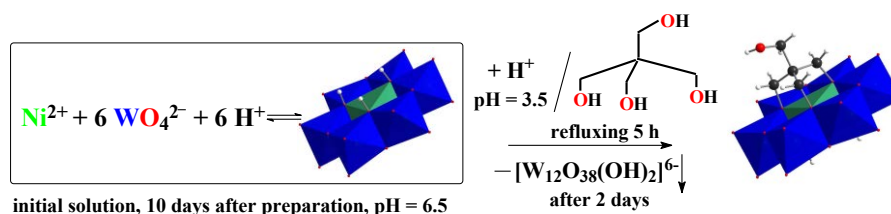
Polyoxometallates (POMs) are an exceptional brand of coordination compounds consisting of early transition metal atoms linked by shared oxygen atoms. [1] Due to their wide range of size, structure and composition, they possess unique thermal, redox, magnetic, optical and bioactive properties and exhibit an enormous potential for application in various fields. [2] The design of organically functionalized (inorganic) POM hybrids via a controllable synthesis has gained much attention since the combination of organic and inorganic components into one single compound provides new properties that benefit from the strengths of both units for multi-functional hybrid materials. [3-4] The controllable synthesis of functionalized Anderson-type polyoxomolybdates (POMo) has gained much attention [5-8] since the first hybrid structure was described in 2002 [5]. This functionalization is achieved by replacing three or six protons of the B-type Anderson-structure $[\text{M}(\text{OH})_6\text{Mo}_6\text{O}_{18}]^{n-}$ ($\text{M} = \text{Zn}^{2+}, \text{Ni}^{2+}, \text{Cr}^{3+}, \text{Mn}^{3+}, \text{Al}^{3+}, \text{Fe}^{3+}, \text{Ga}^{3+}$), which are attached to the $\mu_3\text{-O}$ or even to the less basic $\mu_2\text{-O}$ atoms, with organic tris-ligands. [9] However, to the best of our knowledge nobody succeeded so far in obtaining organically functionalized Anderson-type polyoxotungstates (POTs). The application of $[\text{TeW}_6\text{O}_{24}]^{6-}$ (TEW, A-type Anderson-POT) has recently been expanded to its successful use as an additive in protein crystallization. [10-12] Here, $[\text{TeW}_6\text{O}_{24}]^{6-}$ demonstrated superiority over other POM archetypes owing to its good water solubility, pH-stability, disk-shape structure and relatively high negative charge. We report the first synthesis and characterization of a tris-functionalized anion, $[\text{Ni}(\text{OH})_3\text{W}_6\text{O}_{18}(\text{OCH}_2)_3\text{CCH}_2\text{OH}]^{4-}$ (**NiW₆-Tris-CH₂OH**).

II. Results and Discussions

NiW₆-Tris-CH₂OH is assembled by a condensation reaction of Tris-CH₂OH with the $[\text{Ni}(\text{OH})_6\text{W}_6\text{O}_{18}]^{4-}$ anion in an acidified aqueous solution (Scheme 1). Initially, an aqueous solution of $\text{Ni}^{2+}\text{-WO}_4^{2-}\text{-H}^+$ with a molar ratio of 1:6:6 (Ni:W:H⁺) at pH 6.5 was prepared. The reaction mixture was kept 10 days at ambient conditions in order to increase the concentration of $[\text{Ni}(\text{OH})_6\text{W}_6\text{O}_{18}]^{4-}$. The pH of the obtained blue solution was reduced to 3.5 with diluted nitric acid. Tris-CH₂OH was added in fivefold excess before refluxing the solution for 5 h followed by the addition of tetramethylammonium (TMA) chloride as counter ions. After filtration of the reaction solution a salt has been isolated and identified by single-crystal X-ray diffraction measurements and IR spectroscopy as metatungstate $\text{TMA}_6[\text{W}_{12}\text{O}_{38}(\text{OH})_2]$. From the blue mother liquor the single-side tris-functionalized Anderson-type $[\text{Ni}(\text{OH})_3\text{W}_6\text{O}_{18}(\text{OCH}_2)_3\text{CCH}_2\text{OH}]^{4-}$ has been obtained in a quite good yield of 55 %.

$\text{Na}_2[\text{TMA}]_2[\text{Ni}(\text{OH})_3\text{W}_6\text{O}_{18}(\text{OCH}_2)_3\text{CCH}_2\text{OH}]\cdot 9\text{H}_2\text{O}$ crystallizes in the triclinic space group *P1*. The structure is composed of a **NiW₆-Tris-CH₂OH** anion, two tetramethylammonium and two sodium cations. **NiW₆-Tris-CH₂OH** shows the common Anderson heteropolyanion structure which consists of six WO_6 octahedra arranged hexagonally around the central $\{\text{NiO}_6\}$ octahedron. Tris-CH₂OH replaces three protons from the $\text{Ni}(\text{OH})_6$ core in order to attach to the disk shape anion. The Ni–O bond lengths are in the range from 2.018(11) to 2.042(15) Å and the $\mu_3\text{-O-C}$ bond lengths are in the range from 1.373(2) to 1.389(2) Å, which is in good agreement with the corresponding bond lengths of $[\text{H}_2\text{NiMo}_6\text{O}_{18}\{(\text{OCH}_2)_3\text{CCH}_2\text{OH}\}_2]^{2-}$. [6] The **NiW₆-Tris-CH₂OH** anion interacts with sodium counter cations via their W=O terminal oxygen atoms (O7, O11), hence the coordination sphere of Na^+ consists of two oxygen atoms from two neighboring polyanions and three water molecules exhibiting trigonal bipyramide geometry. That way, alternate heteropolyanions and sodium NaO_5 polyhedra form parallel chains interacting through intermolecular hydrogen bonds.

IR spectroscopy was applied to investigate the anion **NiW₆-Tris-CH₂OH**. The characteristic peaks of the core structure are all in agreement with the peaks observed in the spectrum of $\text{Na}_4[\text{Ni}(\text{OH})_6\text{W}_6\text{O}_{18}]\cdot 16\text{H}_2\text{O}$. [13] The stretching vibrations of the terminal W=O units appear at 955 and 940 cm^{-1} . The peaks at 884 cm^{-1} and in the region of 470–750 cm^{-1} correspond to the antisymmetric and symmetric deformation vibrations of W–O–W and W–O–Ni bridging fragments. The three peaks appearing at 1105, 1072 and 1035 cm^{-1} could be assigned to C–O stretching vibrations, indicating the successful grafting of Tris-CH₂OH. The ESI-MS spectrum of **NiW₆-Tris-CH₂OH** demonstrates its complex character and exhibits a peaks envelope at $m/z = 828.8$ and $m/z = 839.9$ which can be unambiguously assigned to the double charged anions $\text{Na}_{2-x}\text{H}_x[\text{Ni}(\text{OH})_3\text{W}_6\text{O}_{18}(\text{OCH}_2)_3\text{CCH}_2\text{OH}]^{2-}$ ($x = 0, 1$; calculated mass of 828.8 and 839.9) indicating the presence of the intact cluster in the solution.



Scheme 1. The synthesis of **NiW₆-Tris-CH₂OH**; color code: WO₆, blue octahedra; NiO₆, green octahedron; O, red; C, black; H, white

To investigate the interactions between the negatively charged Anderson-tungstate anions and the positively charged surface regions in human serum albumin (HSA), zeta potential measurements on a series of POTs with Ni, Cr and Te as heteroatom ([Ni(OH)₆W₆O₁₈]^{4−}, [Cr(OH)₃W₆O₂₁]^{6−}, [TeW₆O₂₄]^{6−}) and the tris-functionalized product **NiW₆-Tris-CH₂OH** were applied. The zeta potential was measured in NaOAc buffered (50 mM, pH 4.0) solutions containing 1 mg·mL^{−1} (0.015 mM) of HSA. The concentration of heteropolyanions {XW₆} was varied from 0 to 1 mM and all solutions were incubated overnight at 4 °C prior to the measurements. The molar ratio between protein and {XW₆} anions varied from 1:0 to 1:67. The results are illustrated in Figure 1 and indicate a progressive decrease of the zeta potential of the surface of HSA with increasing POT concentration for all compounds. The slightly lower concentration of **NiW₆-Tris-CH₂OH** for charge inversion in comparison to that of [Ni(OH)₆W₆O₁₈]^{4−} may be caused by additional interaction between the OH functionality and the protein. The interactions of triply charged Anderson-type POMos with bovine serum albumin also showed charge inversions of BSA at low concentrations of anions decorated with Tris-CH₂OH bearing a high negative surface charge. [8]

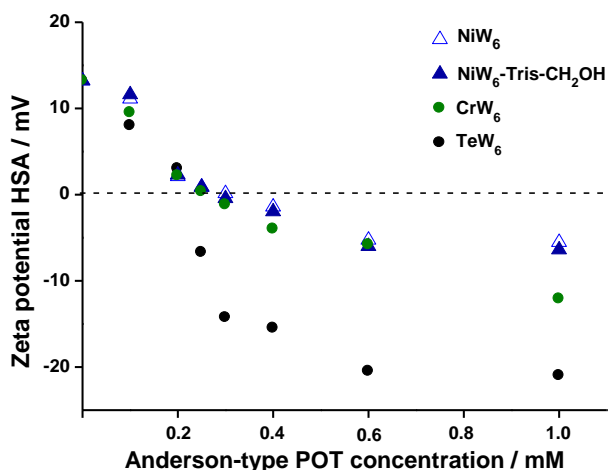


Fig. 2. The zeta potential of HSA as a function of Anderson POT concentration

Conclusion

In summary, 14 years after the first successful tris functionalization of an Anderson type POMo, **NiW₆-Tris-CH₂OH** is the first example of a covalently modified

Anderson-type heteropolytungstate. The hydrated sodium tetramethylammonium salt of **NiW₆-Tris-CH₂OH** has been synthesized in good yields and has been extensively characterized in solid state and in solution. Zeta potential measurements performed on **NiW₆-Tris-CH₂OH** in the presence of HSA demonstrated its applicability to induce charge inversion. The introduction of tris-ligand to Anderson-type POTs suggests existence of a rich tris-functionalized POT chemistry that will be elucidated in the future. The proposed synthesis strategy opens a route for new multi-functional organic-inorganic hybrid materials for various applications.

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