

A phosphonate-lanthanoid polyoxometalate coordination polymer: $\{\text{Ce}_2\text{P}_2\text{W}_{16}\text{O}_{60}\text{L}_2\}_n$ zipper chains

Received 00th January 20xx,
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

$\{\alpha_2, \alpha_2'\text{-P}_2\text{W}_{16}\text{O}_{60}\}$ polyoxotungstate cluster units featuring phenylphosphonates and Ce^{III} ions embedded into the segregated lacunary sites of the cluster shell organize into the first coordination polymer of a polyoxometalate functionalized by both organophosphonate and lanthanoid. Inter-cluster $\text{Ce}-\text{O}=\text{W}$ links result in double-chains, with $\{\text{Ce}^{\text{III}}_2(\alpha_2, \alpha_2'\text{-P}^{\text{V}}_2\text{W}^{\text{VI}}_{16}\text{O}_{60})\text{L}_2\}$ cluster units oriented alternately perpendicular to the chain propagation direction, akin to the protruding teeth of a zipper.

Polyoxotungstates (POTs) represent polynuclear oxo-clusters of $\text{W}^{\text{VI}}/\text{W}^{\text{V}}$ centers of general composition $[\text{X}_x\text{W}_y\text{O}_z]^{n-}$, where X is a heteroelement (typically P^{V} , Si^{IV} , Ge^{IV} , B^{III} etc.). Removal of one or more W centers from their closed (i.e. highly condensed) metal oxide shells results in vacant sites (lacuna) defined by multiple nucleophilic O atoms, rendering lacunary POTs as excellent, structurally rigid multidentate O donor ligands. In particular, these thermally and redox-stable metal oxide matrices provide suitable scaffolds for coordination of Ln^{III} ions and stabilization of various coordination geometries, with coordination numbers ranging from 6 to 11.^{1–6} The electronic, magnetic, catalytic, photoluminescent and solubility properties of Ln-POTs can be further tuned by introduction of various organogroups in these inorganic systems.^{7–22} Among them, carboxylates are by far the most investigated,^{7–8,12–16} yet they are bound to the Ln^{III} ions through just one or two O atoms, and tend to readily dissociate from the Ln-POT framework in solutions, sometimes leading to decomposition of the entire Ln-POT entity. In contrast, organoelement groups RXO_y^{n-} ($\text{X} = \text{P}$,^{17–20} B ,²¹ $y = 3$; Sn ,¹⁵ $y = 4$), able to anchor to both $\text{Ln}^{\text{III/IV}}$ and W^{VI} sites via three oxygen atoms, allow the design of stable organo-Ln-POT systems.

However, RXO_y -decorated Ln-POTs still remain scarce; only very few examples of such species are known: the propeller-shaped aminomethylphosphonate-functionalized $[\text{Dy}^{\text{III}}_9(\text{CO}_3)_3(\text{H}_3\text{NCH}_2\text{PO}_3)_2(\text{H}_2\text{O})_{12}(\text{PW}_{10}\text{O}_{37})_6]^{35-}$ exhibiting single-molecule magnet behavior;¹⁷ a boronic acid-decorated Ln-POT forming a 2D structure, $\text{H}_3[\{\text{Eu}_2(3\text{-PyB}(\text{OH})_2)(\text{H}_2\text{O})_{11}\}[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]\cdot 11\text{H}_2\text{O}$, that exhibits stronger photoluminescence vs. the corresponding Eu-POT not bearing organic functional groups;²¹ methyltin/isonicotinate/acetate-supported polyoxotellurites of interest for the design of POT-based optical nanomaterials.¹⁵

One especially valuable approach to the synthesis of bi-functionalized POTs concerns their stepwise functionalization. Recently, we focused on a post-functionalization study of the phenylphosphonate-decorated Wells-Dawson-type POTs $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}(\text{PhPO})_2]^{6-}$ ($\{\alpha_2\text{-P}_2\text{W}_{17}(\text{PhP})_2\}$)²³ as rare examples of readily available, water soluble and solution-stable (at room temperature) organophosphonate-functionalized POTs with lanthanoid cations. We discovered that reactions of $\{\alpha_2\text{-P}_2\text{W}_{17}(\text{PhP})_2\}$ with Dy^{III} and Y^{III} ions result in the removal of one of the W^{VI} centers and, thus, in formation of a second, structurally separated vacancy (i.e. lacuna site) in the POT framework, able to bind heterometals. Importantly, this structural transformation of the POT occurred without loss of the primary organic (phenylphosphonate) groups. Both vacancies belong to the two outer ‘cap’ groups of the Wells-Dawson structure, which are separated by two W_6 ‘belt’ segments. The second vacant site is condensed to two phenylphosphonate ligands, and its appearance leads to the previously unknown $\{\alpha_2, \alpha_2'\text{-P}_2\text{W}_{16}\text{O}_{60}\}$ POT isomer. As a result, solution-stable dimeric $[\{(\text{H}_2\text{O})_x\text{Ln}_2(\alpha_2, \alpha_2'\text{-P}_2\text{W}_{16}\text{O}_{60})(\text{PhPO})_2\}]^{8-}$ polyanions ($\text{Ln} = \text{Dy}^{\text{III}}$ (**2**) and Y^{III} (**3**)) have been isolated as the hydrated caesium/potassium salts $\text{Cs}_{7.5}\text{K}_{0.5}[\{(\text{H}_2\text{O})_7\text{Dy}^{\text{III}}_2(\alpha_2, \alpha_2'\text{-P}_2\text{W}_{16}\text{O}_{60})(\text{C}_6\text{H}_5\text{PO})_2\}] \cdot 42\text{H}_2\text{O}$ and $\text{Cs}_{7.5}\text{K}_{0.5}[\{(\text{H}_2\text{O})_{7.7}\text{Y}^{\text{III}}_2(\alpha_2, \alpha_2'\text{-P}_2\text{W}_{16}\text{O}_{60})(\text{C}_6\text{H}_5\text{PO})_2\}] \cdot 38.6\text{H}_2\text{O}$.²² Upon further investigation of the $\text{Ln}^{\text{III}}/\{\alpha_2\text{-P}_2\text{W}_{17}(\text{PhP})_2\}$ reaction system we have noticed that addition of a slight excess of a Ln^{III} salt results in barely soluble products with presumably polymeric structures. By adjusting the reaction

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Electronic Supplementary Information (ESI) available: Experimental and synthesis details, structural illustrations, powder X-ray diffraction data, IR spectra, TGA/DTA curves, solid-state UV-Vis spectrum. See DOI: 10.1039/x0xx00000x

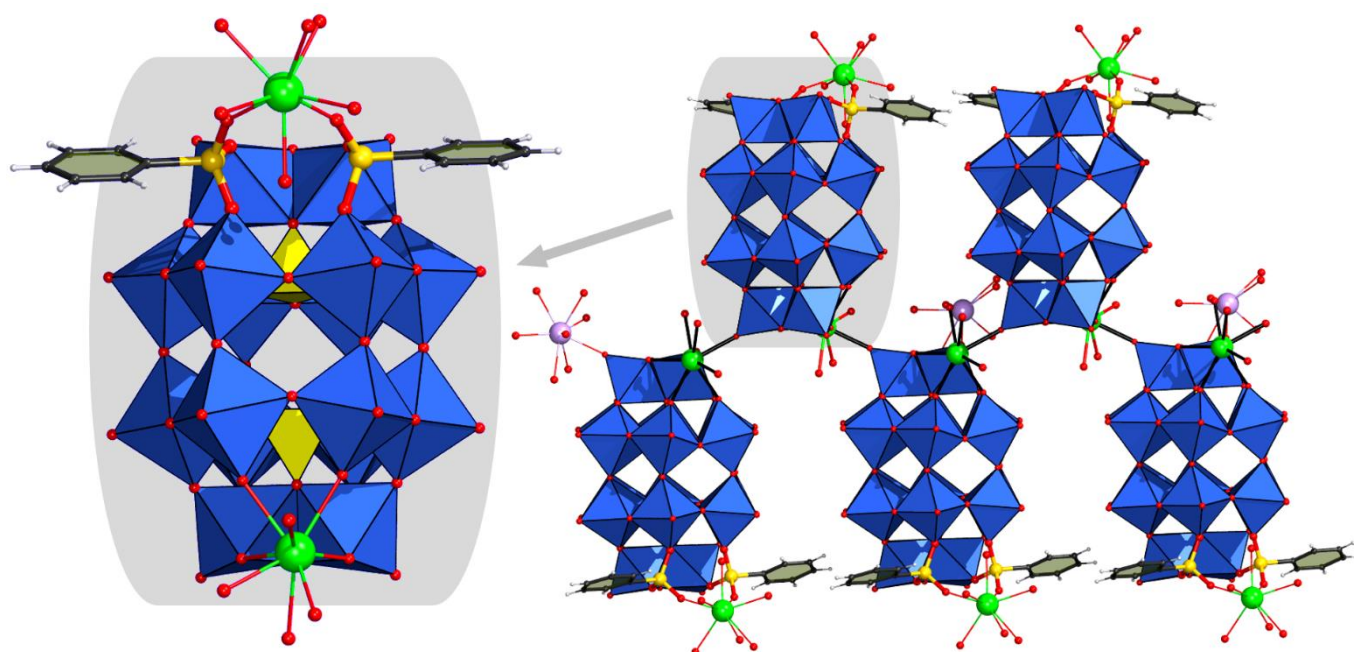


Figure 1 Structure of the monomeric unit $\{(H_2O)_{9.25}Ce_2(\alpha_2\alpha_2'-P_2W_{16}O_{60})(C_6H_5PO)_2\}^{4-}$ (left) and a fragment of the double-chain in **D-1** (right). The inter-cluster Ce–O(W) bonds forming the backbone of the 1D polymer **1** are highlighted as bold black lines. Color code: $\{WO_6\}$: blue octahedra, $\{PO_4\}$: yellow tetrahedra; Ce: green, P: yellow, C: black, H: white; O: red spheres. The Ce_C counteranions (s.o.f. 0.5) are shown as lilac spheres.

and crystallization conditions we were now able to isolate pure, single-crystalline material of the Ce^{III} derivative.

The title compound, isolated as the dimethylammonium salt $[(CH_3)_2NH_2]_{2.5}[Ce^{III}(H_2O)_{4.5}]_{0.5}[(H_2O)_{9.25}Ce^{III}_2(\alpha_2\alpha_2'-P_2W_{16}O_{60})(C_6H_5PO)_2] \cdot 17.5H_2O$ (**D-1**), was obtained by reacting $\{\alpha_2-P_2W_{17}(PhP)_2\}$ with $CeCl_3 \cdot 7H_2O$ in a ca. 1 : 3 molar ratio in water at room temperature (pH 2.6) and fully characterized in the solid state via single crystal and powder (Fig. S1) X-ray diffraction, FT-IR spectroscopy (Fig. S6), thermogravimetric analysis (Fig. S7), solid-state UV-Vis spectroscopy (Fig. S8) and SQUID magnetometry.

D-1 crystallizes in the monoclinic space group $C2$ and comprises a 1D coordination polymer based on $\{(H_2O)_{9.25}Ce^{III}_2(\alpha_2\alpha_2'-P_2W_{16}O_{60})(C_6H_5PO)_2\}_n^{4n-}$ (**1**) double chains, with the elongated POT units oriented in an alternating zig-zag fashion reminiscent of a zipper. Neighboring clusters are directly linked via Ce–O=W bridges, in contrast to the vast majority other coordination networks of polyoxometalates where polyanions are typically interlinked by separate heterometal complexes that bind to terminal oxygen sites of two (or more) adjacent clusters. The assembly of **1** proceeds via the highly unusual formation of an additional lacunary site in the pre-functionalized $[\alpha_2-P_2W_{17}O_{61}(C_6H_5PO)_2]^{6-}$ precursor upon reaction with Ce^{III} cations, surprisingly without loss of the two phenylphosphonate groups.

The structure of each monomeric $\{(H_2O)_{9.25}Ce^{III}_2(\alpha_2\alpha_2'-P_2W_{16}O_{60})(C_6H_5PO)_2\}^{4-}$ unit can be formally derived from the “parent” Wells-Dawson $[\alpha-P_2W_{18}O_{62}]^{6-}$ structure composed of two central tetrahedral PO_4 groups surrounded by eighteen

corner- and edge-sharing $W^{VI}O_6$ octahedra, which are arranged in two central $\{PW_6\}$ “belts” and two $\{W_3\}$ “caps” (see Figure S2, left).²⁴ In the precursor $\{\alpha_2-P_2W_{17}(PhP)_2\}$ one of the W^{cap} sites is removed and two phenylphosphonate groups condense to the resulting O_4 lacunary site; each P atom binds to two O atoms of the lacuna site as well as to a terminal O^P atom and a phenyl group (see Figure S2, middle).²³ In **1** one of the Ce^{III} ions (Ce_A) coordinates to these two O^P atoms (Ce_A-O^P : 2.34(2) – 2.42(2) Å) as well as six terminal water molecules (or, precisely, 5.75 as one of the O atoms of the aqua ligands has a site occupancy factor (s.o.f.) of 0.75), Ce_A-O : 2.47(4) – 2.64(4) Å. As such, the coordination number (CN) of Ce^{III} ions of this structural type (Ce_A) is either 7 with distorted capped octahedral coordination environment or 8 with dodecahedral coordination geometry in 25 and 75 % of the monomeric $\{(H_2O)_{9.25}Ce^{III}_2(\alpha_2\alpha_2'-P_2W_{16}O_{60})(C_6H_5PO)_2\}^{4-}$ units, respectively (Figure 1 and S2, right). In the former case (CN = 7) the two O^P atoms are located on the trigonal face of the octahedron which is opposite to the “capping” $O26C$ center (one aqua ligand disordered over two closely spaced positions). For CN = 8 the geometry of the Ce_AO_8 polyhedron is slightly distorted from the ideal dodecahedral D_{2d} symmetry towards D_2 symmetry which can be also considered as an intermediate coordination geometry between octahedron and square antiprism,²⁵ which in **1** is still much closer to the dodecahedral environment (Figure S3).

As mentioned above, the reaction with Ce^{III} ions results in the removal of one of the $W=O$ groups from the opposite $\{W_3\}$ “cap” in $\{\alpha_2-P_2W_{17}(PhP)_2\}$, generating a second lacuna site and the $\{\alpha_2\alpha_2'-P_2W_{16}O_{60}\}$ framework with idealized C_s symmetry. The

four O atoms of the second lacunary site bind to a single Ce^{III} ion of the second type (Ce_B , $\text{Ce}_\text{B}-\text{O}$: 2.478(19) – 2.559(19) Å). Ce_B binds to terminal aqua ligands ($\text{Ce}_\text{B}-\text{O}$: 2.52(2) – 2.69(3) Å) and to an O atom of a neighboring $\{(\text{H}_2\text{O})_{9.25}\text{Ce}^{\text{III}}_2(\alpha_2, \alpha_2'-\text{P}_2\text{W}_{16}\text{O}_{60})(\text{C}_6\text{H}_5\text{PO})_2\}^{4-}$ unit ($\text{Ce}_\text{B}-\text{O}$: 2.437(18) Å, see Figure 1. $\text{CN}(\text{Ce}_\text{B})$ varies from 8 (square antiprism) to 9 (capped square antiprism) due to partial disorder of two of its aqua ligands (s.o.f. 0.75).

To the best of our knowledge, the formation of **1** from $\{\alpha_2-\text{P}^{\text{V}}\text{W}_{17}(\text{PhP})_2\}$ and Ce^{III} is just the second example for the design of additional lacunary sites in pre-functionalized POTs without loss of primary functional groups, following our recently communicated polyanions **2** and **3** based on similar $\{(\text{H}_2\text{O})_n\text{Ln}^{\text{III}}_2(\alpha_2, \alpha_2'-\text{P}_2\text{W}_{16}\text{O}_{60})(\text{C}_6\text{H}_5\text{PO})_2\}^{4-}$ structural units.²² A key factor apparently is the sufficiently large size of the Ln^{III} ions and, subsequently, their ability to efficiently stabilize the second lacunary site as well as to entangle dissociation of the phenylphosphonate groups, possibly by formation of a larger $\{(\text{H}_2\text{O})_n\text{Ln}^{\text{III}}(\text{C}_6\text{H}_5\text{PO})_2\}$ entity by altogether four O atoms. Removal of this entity should be more complex than dissociation of the separate organophosphonate groups anchored by only two oxygens. Such process does not occur if transition metal ions such as Mn^{II} , Co^{II} and Zn^{II} are used instead under otherwise similar reaction conditions, and only complexes of $\{\alpha_2-\text{P}_2\text{W}_{17}(\text{PhP})_2\}$ could be obtained according to report of Cameron *et al.*²⁶

In contrast to **2** and **3**, where the $\{(\text{H}_2\text{O})_n\text{Ln}^{\text{III}}_2(\alpha_2, \alpha_2'-\text{P}_2\text{W}_{16}\text{O}_{60})(\text{C}_6\text{H}_5\text{PO})_2\}^{4-}$ units are arranged into discrete dimers, the introduction of Ce^{III} in **1** leads to infinite double chains (Figure 1). The interconnection of the monomers in the chain is achieved via coordination of a terminal O atom of a W^{cap} center from one monomeric unit by the Ce_B center of a neighboring monomeric unit. Here, the organofunctionalized parts of the neighboring monomeric fragments are directed opposite to each other (Figure 1). In the crystals of **D-1** the chains of **1** run along *b* and the polyanions both within the chain and in the neighboring chains are arranged alternately (Figure 2).

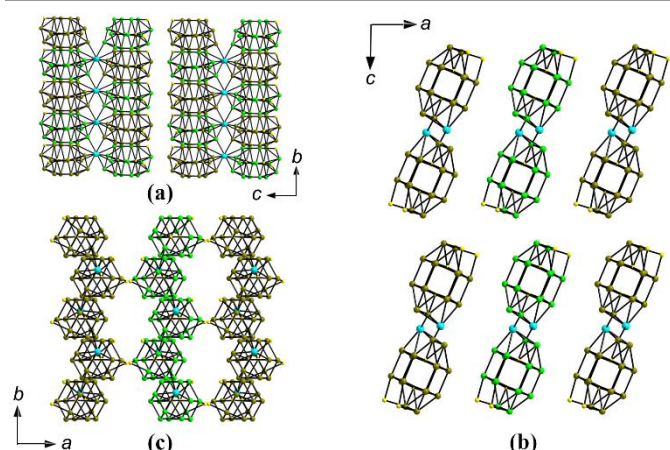


Figure 2. Simplified representation of packing of the infinite chains **1** (only skeletons of W, Ce and P centers are shown): views along crystallographic *a* (a), *b* (b) and *c* (c) axes. Color code: Ce: cyan, P: yellow spheres. W sites of neighboring chains are shown as lime green and as green spheres for clarity.

Interestingly, the phenyl rings in the structure of **D-1** are all nearly coplanar, although there are no intra- and inter-chain $\pi\cdots\pi$ stacking interactions (the closest intra-chain and inter-chain distances between the centers of neighboring phenyl rings amount to 7.02 Å and 8.69 Å, respectively), nor are there $\pi\cdots\pi$ cation interactions. The two phenyl rings of a given monomeric unit lie approximately in the plane formed by two P^{V} of the phenylphosphonate groups and two O atoms of the $\{\text{W}_2\}$ “cap” bound to these P^{V} centers. This is in contrast to **CsK-2** and **CsK-3** where the phenyl rings of the phenylphosphonates in one monomeric unit are rotated by *ca.* 65° relative to each other (Figure S4).

There are also Ce^{III} ions of a third type (Ce_C , lilac spheres in Figure 1) in **D-1**. Every Ce_C cation coordinates weakly to the remaining terminal O atom of the $\{\text{Ce}_\text{B}\text{W}_2\}$ “cap” that is not coordinated to Ce_B ($\text{Ce}_\text{C}-\text{O}$: 2.57(2) Å), and binds terminal aqua ligands ($\text{Ce}_\text{C}-\text{O}$: 2.35(4) – 2.54(5) Å). The s.o.f. of the Ce_C position is only 0.5, meaning that such cations are grafted only to one half of polyanions. Considering this fact, combined with only one weak bond of $\text{Ce}_\text{C}^{\text{III}}$ cation to the monomeric unit and since these Ce^{III} ions do not participate in the binding of the monomeric units into the polymeric framework, we consider Ce_C as counteranions.

Thus, **1** represents the first coordination polymer comprising $\{\alpha_2, \alpha_2'-\text{P}_2\text{W}_{16}\}$ moieties and, following **2** and **3**, just a third example containing this $\{\text{P}_2\text{W}_{16}\}$ isomer. Note that all other known $\{\text{P}_2\text{W}_{16}\}$ complexes constitute either a $\{\alpha_2, \alpha_2'-\text{P}_2\text{W}_{16}\}$ isomer, where the both W^{VI} centers are removed from the same $\{\text{W}_3\}$ “cap” of $\{\alpha-\text{P}_2\text{W}_{18}\}$,²⁷ or $\{\alpha_1, \alpha_1'-\text{P}_2\text{W}_{16}\}$, where neighboring W sites are removed from the two $\{\text{PW}_6\}$ “belts”²⁸ (Figure S5). Nevertheless, given that the isolation of **D-1** requires only a slight modification of the synthesis approach leading to **CsK-2** and **CsK-3** suggests that the chemistry of the $\{\alpha_2, \alpha_2'-\text{P}_2\text{W}_{16}(\text{PhP})_2\} / \text{Ln}^{\text{III}}$ reaction system could be potentially as rich in terms of different modes of mutual interconnections of the Ln-POT units as the chemistry of $\{\alpha_2-\text{P}_2\text{W}_{17}\} / \text{Ln}^{\text{III}}$ complexes, which exhibits a vast amount of discrete and polymeric structures based on 1:1, 1:2, 2:2 as well as 3:3 Ln-POT entities.²⁹

The magnetic susceptibility of **D-1** is shown in Figure 3 as $\chi_\text{m}T$ vs. *T* plot at 0.1 T. At 290 K, the $\chi_\text{m}T$ value of 1.77 cm³ K mol^{−1} falls within the expected³⁰ range of 1.65–1.95 cm³ K mol^{−1} for 2.5 Ce^{III} centers. Upon cooling the compound, $\chi_\text{m}T$ continuously decreases due to the thermal depopulation of the 14 (= 2*J*+1) *m_J* energy states of a 4*f*¹ valence electron configuration split by ligand field and spin-orbit coupling. At 2.0 K, $\chi_\text{m}T$ reaches a value of 0.70 cm³ K mol^{−1}. The field dependence of the molar magnetization *M_m* at this temperature (Figure 3, inset) displays a linear increase up to about 1.5 T and a subsequently decreasing slope, reaching 1.9 *N_A μ_B* at 5.0 T. This value is slightly larger than 1/3 of the saturation value 2.5×15/7 *N_A μ_B* ≈ 5.4 *N_A μ_B* (*gJ* = 15/7), mostly due to the fact that it represents the mean value (powder sample) of statistically oriented magnetically anisotropic centers.

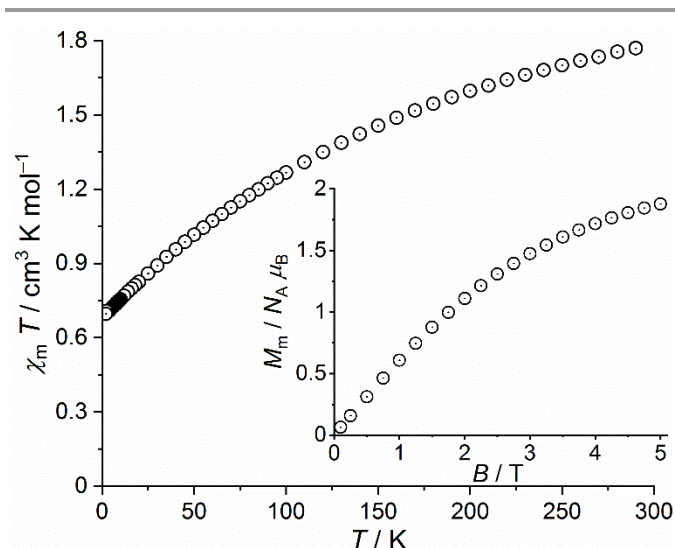


Figure 3. SQUID magnetometry data of **D-1**: temperature dependence of $\chi_m T$ at 0.1 T; inset: molar magnetization M_m vs. magnetic field B at 2.0 K.

Conclusions

The first coordination polymer based on polyoxometalate units functionalized with both organophosphonate moieties and lanthanoid ions was found exclusively for cerium as lanthanoid. Contrary to numerous heterometal-functionalized polyoxometalate network structures, the inter-cluster links between the monomeric $\{(H_2O)_8Ce^{III}_2(\alpha_2, \alpha_2'-P_2W_{16}O_{60})(C_6H_5PO)_2\}^{4-}$ constituents of the double chains in **D-1** do not require additional lanthanoid centers, but are achieved by coordination of an O atom of the POT of one monomer by a Ce^{III} ion fully incorporated in the neighboring building unit, i.e. by direct coordinative links between Wells-Dawson-type POT units. The formation of **1** proceeds via generation of an additional lacunary site in pre-functionalized polyanions, which occurs without loss of the functional organic groups. Surprisingly, although fully structurally exposed in **D-1**, the phenyl groups of the organophosphonates do not exhibit any $\pi \cdots \pi$ or $\pi \cdots \pi$ -cation interactions and as such apparently play no competing role in the organization of the cluster units in the solid state. The $\{(H_2O)_8Ce^{III}_2(\alpha_2, \alpha_2'-P_2W_{16}O_{60})(C_6H_5PO)_2\}^{4-}$ building blocks in **1** represent just the third example of polyanions based on the $\{\alpha_2, \alpha_2'-P_2W_{16}\}$ motif. Based on all these findings, we expect that appropriate modification of reactions conditions may allow formation of a considerable variety of bifunctionalized $\{\alpha_2, \alpha_2'-P_2W_{16}\}$ derivatives with discrete and extended structures and potentially also interesting magnetic and catalytic properties.

We acknowledge financial support by Forschungszentrum Jülich, EU ERC 308051 - MOLSPINTRON and German Science Foundation (Grant DFG-IZ-60/3-1 (N. V. I.)). W. W. is thankful to the China Scholarship Council (CSC) for a doctoral fellowship.

Conflicts of interest

There are no conflicts to declare.

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