

Route for the Elaboration of Functionalized Hybrid 3d-Substituted Trivacant Keggin Anions

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Supporting Information

ABSTRACT: On the basis of four examples involving various transition-metal cations and various carboxylic acid derivatives, we have shown that hybrid 3d metal-containing polyoxometalate systems can be easily built under mild conditions.

In the current development of polyoxometalate¹ (POM) chemistry, the establishment of synthetic methodologies for the preparation of well-defined hybrid compounds where organic ligands are directly connected to inorganic polyanions² is of primary importance. Indeed, the development of such systems not only allows the elaboration of species with unprecedented topologies³ but also opens the way to POM materials possessing new functionalities such as specific cell adhesion behavior on a patterned area,⁴ POM-functionalized three-dimensionally (3D) ordered macroporous silica materials,⁵ model systems of photovoltaic cells,⁶ or POMs with intrinsic photochromic properties.⁷ The rational functionalization of several archetypal POM families by organic groups has thus been achieved. We can mention, as striking examples, the extensive studies devoted to the elaboration of organosilyl derivatives of lacunary Keggin or Dawson POMs, of vanadium-substituted Dawson polyanions or Anderson POMs connected to functional organic groups via trisalkoxo ligands, and of organostannic derivatives of Keggin and Dawson polyoxotungstates (POWs).^{2a} However, no general method allowing the functionalization of 3d-substituted POWs under mild conditions has been proposed, although these last complexes constitute one of the most studied POM families for different purposes including magnetism⁸ or catalysis.⁹ Nevertheless, besides a tetrameric cobalt cluster assembled via three diol ligands¹⁰ and a dimeric iron cluster in which the two subunits are connected by hydroxo groups and a hexamethylenetetramine ligand,¹¹ several acetato derivatives of 3d-substituted POMs have been isolated using synthetic procedures performed under atmospheric pressure. Species incorporating divacant¹² or trivacant¹³ Keggin units as well as divacant¹⁴ or hexavacant¹⁵ Dawson ones have thus been structurally characterized. These examples show that the chelating ability, the flexibility, and the diversity of the connecting modes of the acetate ligand make it particularly suitable for their grafting on 3d-substituted POW compounds. In this context, it appears that a possible way for the elaboration of transition-metal-substituted POWs directly connected to organic groups would be the use of substrates possessing at least one carboxylic function. In the present Communication, we

show that such an approach is relevant, as illustrated by the characterization of hybrid systems where the organic substrates are linked to the POM via the inserted 3d centers. The reported systems, which all contain one or several trivacant POMs, include the copper complex $\text{NaK}_4[(\text{A}-\beta\text{-SiW}_9\text{O}_{34})\text{Cu}_4(\text{OH})_3(\text{H}_2\text{O})(\text{H}_3\text{N}(\text{CH}_2)_3\text{COO})_2] \cdot 18\text{H}_2\text{O}$ (**1**) and the cobalt complex $\text{K}_3\{\text{Co}(\text{H}_2\text{O})_5\}_{0.5}[(\text{B}-\beta\text{-SiW}_9\text{O}_{34})\text{Co}_4(\text{OH})_2(\text{H}_2\text{O})_3(\text{H}_3\text{N}(\text{CH}_2)_2\text{COO})_2] \cdot 18\text{H}_2\text{O}$ (**2**), which represent the first POW compounds directly bound to amino acids. In the nickel complex $\text{NaK}_6[(\text{A}-\alpha\text{-SiW}_9\text{O}_{34})\text{KNi}_4(\text{OH})_3((\text{SC}_4\text{H}_3)\text{CH}_2\text{COO})_3] \cdot 18\text{H}_2\text{O}$ (**3**), three electroactive thiophene groups are grafted on the inorganic fragment. In the tetrameric oligomer $\text{K}_{27}\text{Na}_2(\text{Ni}(\text{H}_2\text{O})_6)_{1.5}[\{(\text{A}-\alpha\text{-SiW}_9\text{O}_{34})\text{Ni}_4(\text{OH})_3\}_4(\text{OOC}(\text{CH}_2)_3\text{COO})_6] \cdot 76\text{H}_2\text{O}$ (**4**), six dicarboxylato ligands ensure cohesion between 16 Ni^{II} ions, forming a macromolecular complex.

Complex **1** is synthesized in good yield by mixing in water under mild heating of $[\text{A}-\beta\text{-SiW}_9\text{O}_{34}\text{H}]^{9-}$, Cu^{II} , and γ -aminobutyric acid at pH 7.5. In **1**, a $\{\text{Cu}_4(\text{OH})_3(\text{H}_2\text{O})(\text{H}_3\text{N}(\text{CH}_2)_3\text{COO})_2\}$ tetranuclear cluster caps the trivacant $[\text{A}-\beta\text{-SiW}_9\text{O}_{34}]$ precursor (Figure 1a). Even if no acetato Cu^{II} POM has been reported so far, the topology of the paramagnetic cluster constituting **1** can be compared to that found in the previously reported complexes $[(\text{A}-\alpha\text{-SiW}_9\text{O}_{34})\text{M}_4(\text{OH})_3(\text{CH}_3\text{COO})_3]^{8-}$ ($\text{M} = \text{Co}^{\text{II}}, {}^{13\text{b}}\text{Ni}^{\text{II}13\text{c}}$), which possess a pseudo- C_3 symmetry. For these species, all of the 3d centers are hexacoordinated and the fourth, apical magnetic center is connected to the three cations inserted in the POM via three μ_3 -hydroxo groups and three $\eta^1:\eta^1:\mu_2$ -acetate ligands. In **1**, because of the strong Jahn–Teller effect characterizing cupric ions, the apical Cu^{II} center is only pentacoordinated. It follows that only two amino acids are connected to the POM, which possesses C_s symmetry. Charge considerations indicate that the two amino functions are protonated, in agreement with the pK_a values of such primary amino groups (ca. 10.4) and the pH of the reacting medium. Each alkylammonium group is involved in intermolecular hydrogen bonds with two adjacent POM subunits, with the absence of any intramolecular hydrogen-bond interactions (Figure S11 in the Supporting Information, SI).

Attempts to synthesize related hybrid Cu^{II} POM compounds but with chelating α - or β -amino acids have failed, and indeed UV–vis studies indicate that (a) using the α -amino acid glycine instead of γ -aminobutyric acid, the highly stable mononuclear species $\{\text{Cu}(\text{glycinate})_2\}$ characterized by a band at 640 nm is almost quantitatively formed (Figure 1b, inset) and (b) when the

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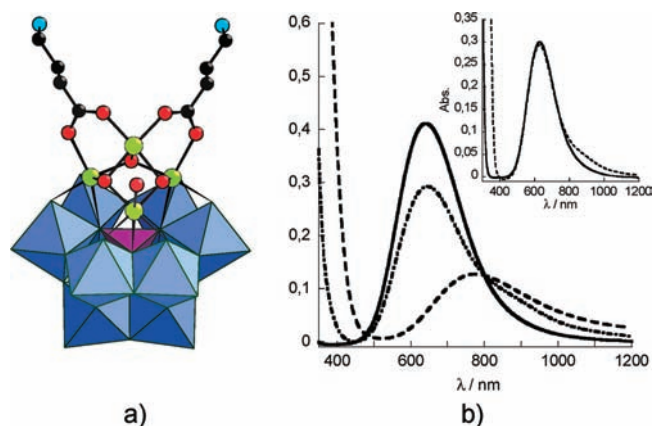


Figure 1. (a) Mixed polyhedral and ball-and-stick representation of complex **1**: blue octahedra, WO_6 ; purple tetrahedron, SiO_4 ; green spheres, Cu; red spheres, O; black spheres, C; blue spheres, N. (b) UV-vis spectra of (i) the reacting media of complex **1** (dashed line), (ii) an analogous mixture but with replacement of γ -aminobutyric acid by β -alanine (dash-dotted line), and (iii) the Cu^{II} / β -alanine system (solid line). Inset: (i) Reacting media of complex **1** but with replacement of γ -aminobutyric acid by glycine (dashed line) and (ii) the Cu^{II} /glycine system (solid line).

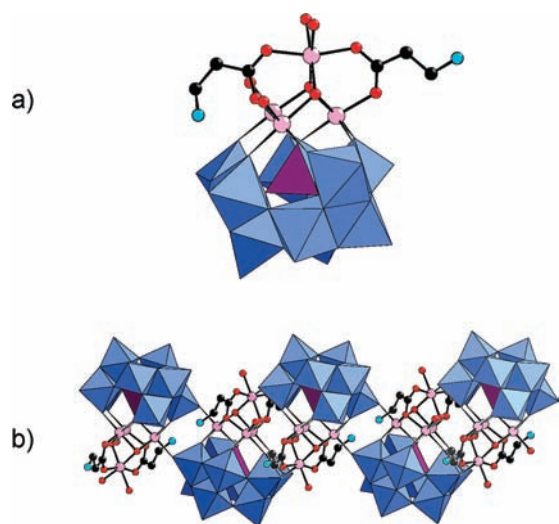


Figure 2. Mixed polyhedral and ball-and-stick representations of (a) the molecular unit constituting **2** and (b) the 1D structure of compound **2**: blue octahedra, WO_6 ; purple tetrahedron, SiO_4 ; pink spheres, Co; red spheres, O; black spheres, C; blue spheres, N.

β -amino acid β -alanine is considered, an equilibrium between POM species and the $\{\text{Cu}(\beta\text{-alanine})_2\}$ complex, which must prevent isolation of a hybrid POM, is observed (Figure 1b). However, noticeably, it must be pointed out that as in **1** the amino acids are connected via the carboxylato groups, with the amino groups being noncoordinated, it must be possible to graft onto the inorganic core constituting this complex a huge variety of organic groups synthesized by prefunctionalization of the γ -aminobutyric acid via the amino fragment.

The grafting of a β -amino acid onto a 3d-substituted POM has been achieved in the presence of Co^{II} . Compound **2** has been obtained by mixing at room temperature the divalent precursor $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{9-}$, Co^{II} , and β -alanine at neutral pH. In **2**, the

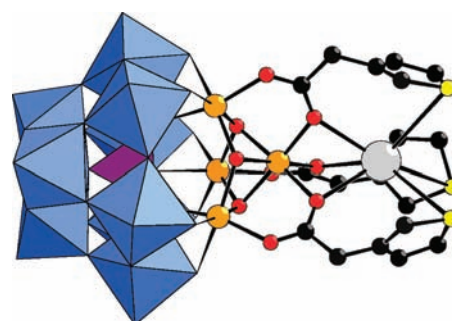


Figure 3. Mixed polyhedral and ball-and-stick representation of complex **3**: blue octahedra, WO_6 ; purple tetrahedron, SiO_4 ; yellow-gold spheres, Ni; gray sphere, K; red spheres, O; black spheres, C; yellow spheres, S.

$\{\text{Co}_4(\text{OH})_2(\text{H}_2\text{O})_3(\text{H}_3\text{N}(\text{CH}_2)_2\text{COO})_2\}$ tetranuclear cluster caps a $[\text{B-}\beta\text{-SiW}_9\text{O}_{34}]$ unit (Figure 2a). Such evolution of the $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{9-}$ ligand in the presence of Co^{II} is not unprecedented.^{13b,16} As in **1**, only two amino acids are connected to the inorganic fragment, but in the case of **2**, this can be attributed to the B-type configuration of the POM ligand, which does not possess C_3 symmetry. Compound **2** contains one protonated $\eta^1:\eta^1:\mu_2$ - β -alanine, involved in intermolecular hydrogen bonds with two adjacent POM subunits, and one protonated $\eta^2:\eta^1:\mu_2$ - β -alanine, involved in both intermolecular and intramolecular hydrogen bonds. It results that each POM is hydrogen-bonded to three adjacent polyanions (Figure SI2 in the SI). Additionally, two Co^{II} centers of the tetranuclear unit are each connected to adjacent POMs, leading to a one-dimensional (1D) zigzag chain arrangement (Figure 2b). The electronic absorption spectrum of the reacting media of **2** is typical of a POM/ Co^{II} species even after 3 days (Figure SI3 in the SI). In contrast, replacement of this amino acid by glycine affords a POM-free Co/glycinate complex (Figure SI4 in the SI). While amino acid/polyoxomolybdate compounds have been reported,¹⁷ no structure of POW grafted by an amino acid has been reported prior to characterization of **1** and **2**. However, the interaction between such entities has been investigated in solution by NMR for a wide variety of amino acids and POMs focusing on lanthanide species, and several propositions concerning their interaction modes have been made.¹⁸ The present report confirms that such an organic ligand is bound to the metal cations via the oxygen atoms and that the amino group is protonated. Besides, in the solid state, the hydrogen-bond interaction mode, which has been deeply discussed, seems dependent on the type of amino acid used. It appears that an increase of the number of carbon atoms between the acid and the amino group favors intermolecular hydrogen-bond interactions. This then supports the assumption that α -amino acids develop intramolecular hydrogen bonds with POMs.^{18b}

Compound **3** (Figure 3) has been prepared at 80 °C by mixing $[\text{A-}\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$, Ni^{II} , and 3-thiopheneacetic acid at pH 7.5. This time, three $\eta^1:\eta^1:\mu_2$ carboxylato groups are connected to a tetranuclear $\{\text{Ni}_4(\text{OH})_3\}$ cluster, leading to the $[(\text{A-}\alpha\text{-SiW}_9\text{O}_{34})\text{KNi}_4(\text{OH})_3((\text{SC}_4\text{H}_3)\text{CH}_2\text{COO})_3]^{7-}$ complex, which possesses pseudo- C_3 symmetry. While the $\{\text{Ni}_4(\text{OH})_3\}$ core is similar to that encountered in other $\{\text{A-SiW}_9\text{O}_{34}\}$ derivatives,^{13c} it differs from the more symmetric cubane-type $\{\text{Ni}_4(\text{OH})_3\}$ capping a $\{\text{A-PW}_9\text{O}_{34}\}$ described by Kortz et al.¹⁹ Furthermore, in **3**, the aromatic rings of the 3-thiopheneacetate groups define a pocket, in which is trapped a potassium ion. This alkaline cation

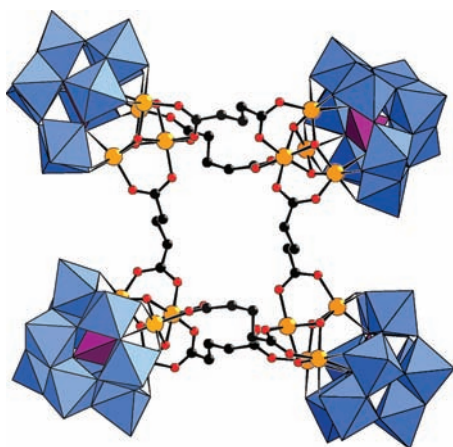


Figure 4. Mixed polyhedral and ball-and-stick representation of **4**: blue octahedra, WO_6 ; purple tetrahedra, SiO_4 ; yellow-gold spheres, Ni; red spheres, O; black spheres, C.

is hexacoordinated with a $\{\text{S}_3\text{O}_3\}$ coordination sphere. Complex **3** illustrates that the presented synthetic strategy not only allows the grafting of amino acids but also the connection of a functional organic group, in the present case an electroactive group.

Compound **4** (Figure 4) has been obtained under heating at 80°C starting from $[\text{A}-\alpha\text{-SiW}_9\text{O}_{34}]^{10-}$, Ni^{II} , and dicarboxylic glutaric acid at pH 8. The topology of the 3d core is highly similar to that found in complex **3**, but the use of dicarboxylate instead of monocarboxylate leads to the formation of a tetrameric oligomer, where the two carboxylate groups of the organic ligand are connected to two adjacent POM units. Thus, our synthetic strategy allows not only the formation of functionalized monomeric POM systems but also the formation of large oligomeric clusters. In $[\{(\text{A}-\alpha\text{-SiW}_9\text{O}_{34})\text{Ni}_4(\text{OH})_3\}_4(\text{OOC}(\text{CH}_2)_3\text{COO})_6\}^{32-}]$, the four subunits adopt an almost planar arrangement, forming a rectangle of ca. $15 \times 25 \text{ \AA}$. The small and long sides of the rectangle correspond to the connection between two subunits via two glutarate connectors and one dicarboxylate ligand, respectively.

In summary, on the basis of four examples involving various transition-metal cations and various carboxylic-based ligands, we have shown that hybrid POM systems with new topologies can be easily built under mild conditions. It must be possible to extend this strategy to other 3d magnetic ions such as Mn^{II} or Fe^{III} because acetate POM derivatives involving these cations have already been obtained.^{14,15} Similarly, because 3d-substituted acetate Dawson POMs with nuclearities up to 28 have been isolated,¹² the use of Dawson ligands instead of Keggin ones must allow one to obtain functionalized clusters of higher nuclearities. Also, the synthetic strategy presented here must be extendable to a huge number of carboxylate organic substrates, allowing one to bring various properties to the synthesized systems. For example, the use of chiral organic groups must afford stereochemical properties to such 3d-substituted hybrid POW systems.²⁰ These topics are currently under investigation in our group.

■ ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data in CIF format, experimental procedures, and Figures S11–S14. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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