Hybrid Polyoxometalates

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Insertion of Amides into a Polyoxometalate**

Joaquim Li, Inga Huth, Lise-Marie Chamoreau, Bernold Hasenknopf, Emmanuel Lacôte,* Serge Thorimbert,* and Max Malacria*

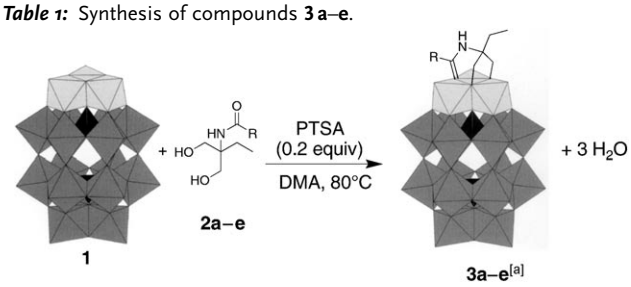
Grafting organic moieties onto polyoxometalates[1] (POMs, polyanionic metal–oxo clusters of early transition metals in their highest oxidation state[2]) is a way to increase the diversity of these inorganic clusters. This aim is of high relevance for the various fields in which POMs are used, as well as for those in which they have shown potential applicability, such as catalysis,[3] materials science,[4] or chemical biology.[5,6] Such hybrids can also be used to build covalent[7,8] or supramolecular networks.[9–11]

Nonetheless, covalent attachment of organic molecules to the polyoxometallic framework does not necessarily lead to mutual influence of the two components of the hybrids on each other (by electronic communication through the covalent organic/inorganic linkages). Despite the considerable existing body of work devoted to the functionalization of POMs,[1,12] deliberate tuning of the hybrid properties by systematic variation of the organic appendage of a given polyoxometallic backbone remains scarce. The imido and diazenido functions in Lindqvist-type molybdates $[Mo_6O_{18}\{NAr\}]^{2-}$ [13] and $[Mo_6O_{18}\{NNAr\}]^{3-}$ [14] (Ar = aryl) present a fully conjugated π-system in the ligand and efficiently transmit the electronic properties of the Ar groups onto the polymolybdate.

Incorporation of tris(hydroxymethyl)methane derivatives has proven a viable route to graft organic groups onto a variety of POMs, such as Lindqvist,[9,15] Anderson,[10,16–18] or Dawson structures.[8,19,20] However, no electronic communication between the ligand substituents and the POM has been established. We present herein a new functionalization of the Dawson-type POM $[P_2V_3W_{15}O_{62}]^{9-}$ **1** with amide derivatives of 2-amino-2-ethyl-1,3-propanediol **2** (see Scheme in Table 1). The new feature of these hybrids is the substitution of a POM oxo ligand with the carbonyl oxygen of the amide function. Incorporation of carbonyl groups into POM frameworks remain rare,[21] and, to our knowledge, ours is the first example of insertion of amides into a POM. Moreover, variation of the amide residue indicated efficient communication of electronic effects between the organic ligand and the inorganic cluster.

The reaction of 2-acetamido-2-ethyl-1,3-propanediol **2a** with $TBA_5H_4[P_2V_3W_{15}O_{62}]$ (TBA = nBu_4N^+) in dimethylacetamide (DMA) yields a functionalized POM, which was subsequently identified to be $[P_2V_3W_{15}O_{59}\{(OCH_2)_2C(Et)NHCOCH_3\}]^{5-}$ **3a** (Table 1). Optimization of the reaction conditions to afford quantitative conversion was achieved by adding a small amount of *para*-toluenesulfonic acid (PTSA) and by steady removal of the formed water under vacuum. **3a** can be handled at air, although it is more sensitive to hydrolysis than triesters $[P_2V_3W_{15}O_{59}\{(OCH_2)_3CR\}]^{6-}$.[20]

Table 1: Synthesis of compounds **3a–e**.



Entry	R	Yield [%]
a	CH_3	85
b	C_6H_4-*p*-NO_2	92
c	C_6H_5	86
d	C_6H_4-*p*-OMe	75
e	C_6H_4-*p*-NEt_2	87

[a] **1** = $TBA_5H_4[P_2V_3W_{15}O_{62}]$; TBA = tetrabutylammonium; PTSA = *para*-toluenesulfonic acid; DMA = dimethylacetamide; **3** = $TBA_5[P_2V_3W_{15}O_{59}\{(OCH_2)_2C(Et)NHCOR\}]$.

3a was characterized by multinuclear NMR, IR, and UV/Vis spectroscopy, ESI mass spectrometry, and single-crystal X-ray diffraction. An AB system around $\delta = 5.5$ ppm, corresponding to the two CH_2O groups in the ^1H NMR spectrum of the product, indicates that these functions are incorporated into the POM as alkoxide ligands to give a diester compound. A symmetry element relates both groups, and, based on previous work on related systems,[8,19,20] they should occupy bridging positions in the V_3 cap. The most striking feature of **3a** is best evidenced by its ESI-MS analysis, which shows that **3a** has one fewer oxygen atom and two fewer negative

[*] J. Li, I. Huth, Dr. L.-M. Chamoreau, Dr. B. Hasenknopf, Dr. E. Lacôte, Dr. S. Thorimbert, Prof. M. Malacria
UPMC Univ Paris 06
CNRS UMR 7201, Institut Parisien de Chimie Moléculaire
4 place Jussieu, 75005 Paris (France)
Fax: (+33) 1 44 27 38 41
E-mail: bernold.hasenknopf@upmc.fr
emmanuel.lacote@upmc.fr
serge.thorimbert@upmc.fr

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charges than the compound would have if the functionalization was solely by alkoxo ligands ($m/z = 1519.4$, 1079.4, and 814.7, corresponding respectively to $\{TBA_2[P_2V_3W_{15}O_{59}\{(OCH_2)_2C(Et)NHCOCH_3\}]\}^{3-}$, $\{TBA[P_2V_3W_{15}O_{59}\{(OCH_2)_2C(Et)NHCOCH_3\}]\}^{4-}$, and $\{[P_2V_3W_{15}O_{59}\{(OCH_2)_2C(Et)NHCOCH_3\}]\}^{5-}$; see the Supporting Information). We attributed this result to the substitution of an oxo ligand of the polyoxometallic framework by the carbonyl oxygen of the amide **2a**. This assumption correlates well with the unusually deshielded ^{1}H NMR signal of the acetate group at $\delta = 2.6$ ppm, whereas an acetamide is usually found around 2 ppm. This deshielding can be explained by the electro-attractive effect of the V^V center linked to the carbonyl oxygen. The amide IR bands shifted to slightly lower wavenumbers from **2a** (1632 cm^{-1}) to **3a** (1624 cm^{-1}), indicating a decrease in bond strength.

The crystal structure analysis (Figure 1) confirmed this coordination mode and revealed that the regioselectivity of the substitution is, as expected, at the three V-O-V bridging

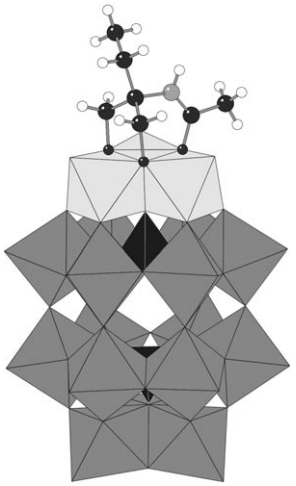

Figure 1. Molecular structure of $[P_2V_3W_{15}O_{59}\{(OCH_2)_2C(Et)NHCOCH_3\}]^{5-}$ (**3a**). Ball and stick: black C, gray N, white H, small black O. Coordination polyhedra: black P, light gray V, dark gray W.

positions in the V_3 cap of the POM. The $V-O_{carbonyl}$ bond lengths are about 0.2 Å longer than those of the μ_2-alkoxide bridging ligands, indicating the weaker coordination of that function. The C–N bond is shorter than in average acetamides (1.26 Å compared to 1.35 Å), whereas the C=O bond is longer (1.30 Å compared to 1.23 Å), showing that extensive delocalization of the nitrogen lone pair occurs. That again is consistent with the ^{1}H NMR spectrum, in which the NH resonance is seen around $\delta = 9.5$ ppm, a chemical shift typical for immonium resonances. Thus the combined analytical data clearly evidence that the solid-state and solution structures are identical.[22]

The functionalized POM **3a** incorporates an sp^2-hybridized carbon with a covalent link of double-bond character to the polyoxometalate framework. This characteristic should allow, to a certain extent, electronic communication between the POM and the π system of the ligand. We therefore synthesized aryl amides **3b–e** (Table 1) and studied the influence of the aryl substitution on the metal ions in these compounds.

The UV/Vis absorption spectra of **3b–e** (see the Supporting Information) display a broad absorption in the near-UV range that corresponds to overlapping LMCT and intraligand π–π* bands, making a direct interpretation impossible. We are currently using density functional (DFT) calculations to deconvolute the spectra and to obtain a better insight into the electronic structure of the C=O–V bonds.

The cyclic voltammograms of compounds **3b–e** are shown in Figure 2 (see the Supporting Information for CV of **3a**). Two redox processes can be distinguished in the range −0.2–

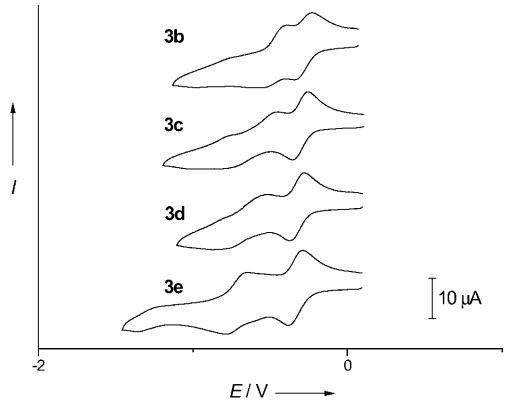

Figure 2. Cyclic voltammograms of **3b–e**. Conditions: POM (0.5 mM); $(nBu_4N)BF_4$ (0.1 M in CH_3CN) as supporting electrolyte; glassy carbon working electrode; potentials relative to Fc^+/Fc; scan rate 100 $mV s^{-1}$.

−0.8 V vs Fc^+/Fc (Fc = ferrocene), in accordance with the nonfunctionalized precursor **1**[23] or the symmetrically functionalized triesters $[P_2V_3W_{15}O_{59}\{(OCH_2)_3CR\}]^{6-}$ (R = CH_3, CH_2OH, NO_2).[20] The first redox process is reversible, as shown by its potential differences between the anodic and cathodic peak (Table 2) and by the dependence of its peak current on the scan speed (see the Supporting Information), whereas the second is pseudo-reversible. These processes should correspond to the reduction of V^V. Most notably, the redox potentials $E_1^{\circ\prime}$ and $E_2^{\circ\prime}$ in the homologous series **3b–e** depend on the aryl substituent. A plot of $E_1^{\circ\prime}$ and $E_2^{\circ\prime}$ as a function of the Hammett parameter σ (Figure 3) gives an excellent correlation, which proves that the electron-donating or attracting power of the aryl substituent allows fine-tuning

Table 2: Comparison of voltammetric data (mV vs Fc^+/Fc) for the first and second redox processes of compounds **3b–e**. The conditions used are the same as in Figure 2.

Compound	1st process		2nd process	
	ΔE_p[a]	$E^{\circ\prime}$[b]	ΔE_p[a]	$E^{\circ\prime}$[b]
3b	98 ± 5	−287 ± 5	212 ± 15	−493 ± 15
3c	85 ± 5	−306 ± 5	224 ± 15	−618 ± 15
3d	84 ± 5	−317 ± 5	160 ± 15	−667 ± 15
3e	90 ± 5	−337 ± 5	122 ± 15	−716 ± 15

[a] $\Delta E_p = E_p^{ox} - E_p^{red}$. [b] $E^{\circ\prime} = (E_p^{ox} + E_p^{red})/2$.

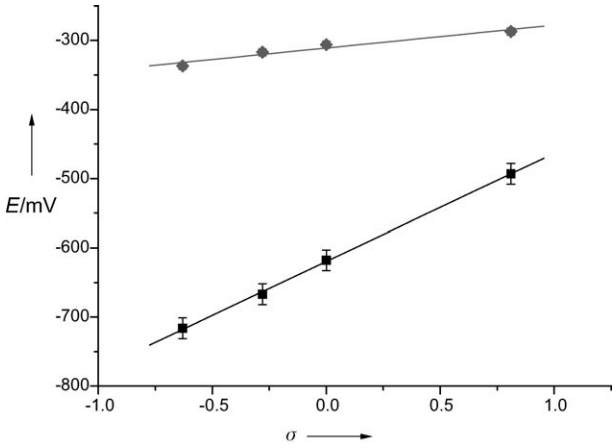

Figure 3. Plot of the potentials for the first (◆) and second (■) redox processes for compounds **3b–e** versus the value of the Hammett parameter (σ) for the *para* substituent on the phenyl ring.

of the chemical properties of the POM. The more electron-rich the aryl group, the more difficult it is to reduce the vanadium ions. Thus, the coordinated amide group efficiently transmits the electronic characteristics of the ligand to the POM.

In summary, we have demonstrated that the Dawson-type tungstovanadate $TBA_5H_4[P_2V_3W_{15}O_{62}]$ efficiently reacts with amide-functionalized diols to give a new type of functionalized POM. The unprecedented substitution of an oxo ligand by the oxygen of an amide function, allows fine-tuning of the redox properties of the entire hybrid POMs by their organic components. Conversely, the electron-attracting properties of the POM are transmitted to the ligand, which might be useful for the tuning of organic structures. We believe that appropriate elaboration of the organic ligand will enable the design of original POM-based redox sensors. Finally, analogous replacement of triol ligands by amide-functionalized diols in other POM structures (Lindqvist vanadates,[15,16] Anderson molybdates[17]) should be possible. Hence, the present example appears to be the prototype of a new family of functionalized POMs. Further in this area will be reported in due course.

Experimental Section

The synthesis of ligands **2a–e** is described in the Supporting Information.

Synthesis of POMs **3a–e**: $TBA_5H_4[P_2V_3W_{15}O_{62}]$ (0.077 mmol; 400 mg), PTSA (0.2 equiv, 2.9 mg), and the desired diol (1.2 equiv) were dissolved in DMA (0.5 mL) in a sealed microwave vial containing a stirrer bar. The solution was stirred and heated under microwave irradiation to 80 °C for 20 min. The reaction mixture was then quickly transferred to a round-bottom flask with a minimal amount of acetonitrile and the combined solvents were removed in vacuo. The crude yellow oil was purified (as described in the Supporting Information) to yield POMs (**3a–d** pale yellow, **3e** brown).

Full analytical data are in the Supporting Information.

CCDC 711854 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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