Post-functionalization of a Photoactive Hybrid Polyoxotungstate

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A new post-functionalization strategy for hybrid polyoxometalate (POM) clusters is presented, whereby the electronic properties and visible-light driven oxidative reactivity of the POM core can be altered by controlled addition of transition metal ions. The structure of three new metal-functionalised derivatives of a phosphonate hybrid-POM are discussed, alongside a comparison of their electrochemical, photo-chemical and photo-oxidative properties.

Introduction

Polyoxometalates (POMs) have attracted increasing interest in recent years as a result of their appealing physical and chemical properties,1 including their reversible multi-electron redox behaviour, photochemical reactivity2 and extraordinary wealth of potential structures and compositions.3 In particular, the ability of POMs to form meta-stable ‘lacunary’ derivatives (where one or more metal sites is selectively hydrolysed to form a reactive vacancy) provides an almost limitless toolbox for the design, synthesis and post-synthetic modification or tuning of new functional materials.4 Indeed, a significant factor in the rapid growth of POM chemistry over the past few decades has been the keen interest in so-called transition metal substituted POMs (TMSPs) which have been explored for a range of magnetic, catalytic and electronic applications.5 Similarly, the ability to tether organic moieties to the lacunary sites of POM clusters6 has offered a means to combine fascinating complimentary functionalities into a single molecular ensemble,7 opening interesting new avenues in biotechnology, supramolecular self-assembly and materials design.8

Recently, we have shown how the coordination of organophosphonate moieties within such vacancies can be used to photo-activate a Dawson-type polyoxotungstate cluster, \( K_6\left[ P_2W_{17}O_{63}(P(O)C_6H_4CO_2H)\right] \) (1) (see Figure 1) under visible light irradiation.9 This approach is particularly interesting as it allows for direct enhancement of the POM’s inherent photoactivity, which involves generation of a highly reactive charge-separated state (incorporating an o xo-centred radical) upon excitation of the O→W LMCT band.2,10 We have also recently demonstrated how this hybridization strategy can be used to directly tune the electronic structure of the POM, allowing a means to controllably alter its electrochemical and photochemical properties.11 This method potentially opens up a range of new possibilities for interesting catalytic functionalities, however, the scope of such work is limited by the difficulty in combining the attractive features of organic-inorganic hybrid POMs with the ability to selectively add function directly to the POM core via coordination of secondary metal ions, or even polynuclear metal complexes.8,12 In effect, this has led to something of an ‘either-or’ problem in the molecular design of new multi-functional POM complexes, where it has proven difficult to combine or reconcile inorganic and organic functionalisation strategies.

Herein, we demonstrate a new post-functionalization approach for organophosphonate hybridized polyoxometalate clusters in which additional transition metal ions may be appended to the hybridized POM core by a facile one-pot reaction strategy. This allows for the modification of both the electronic properties of the POM and its ability to act as a photo-oxidation catalyst in the decomposition of a common textile-industry pollutant.

Results and Discussion

The benzoic acid hybridized organophosphonate-POM, 1, can be synthesized in good yield as previously reported.9 It is interesting to note that this compound was initially envisaged, in-part, to serve as a stable, redox-active building block in the synthesis of new multifunctional molecules, oligomers or coordination polymers, where the appended carboxylate moieties would serve as the primary means of structural expansion. With this in mind, the one-pot reaction of 1 with a series of 1st row transition metals (Mn2+, Co2+ and Zn2+) under variety of conditions was expected to yield at least one, if not more, of the aforementioned complexes. Instead, we identified

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a series of dimeric cluster species in which the bis-phosphonate position, rather than the carboxylate moieties themselves, acted as a coordinating centre for the transition metal cations. Each new species could be synthesised under effectively identical one-pot conditions (see SI) and could be characterized as:

\[ K_2H_4[\text{Zn}(H_2O)_2][P_2W_{17}O_{61}(P=O)C_6H_5(COOH)]_{2+} \cdot 8C_6H_5NO·9CH_3CN \] 2

\[ K_2H_4[\text{Co}(H_2O)_2][P_2W_{17}O_{61}(P=O)C_6H_5(COOH)]_{2+} \cdot 12C_6H_5NO·3CH_3CN \] 3

\[ (\text{Mn}(H_2O)_{6})_2K_2[\text{Mn}_2(OH)_2(H_2O)_4][P_2W_{17}O_{61}(P=O)C_6H_5(COOH)]_{2+} \cdot 3C_6H_5NO·17CH_3CN \] 4

Structural analysis of 2 clearly demonstrates how the neighbouring terminal P=O sites \((d_{P=O(avg)} = 1.50 \text{ Å})\) on the bis-phosphonate moiety are able to act as a bidentate coordinating site towards a single Zn\(^{2+}\) ion, forming a 1:1 dimeric complex between the two hybrid-PO\(M\) units. In this case, the Zn\(^{2+}\) cation bridges two POM sub-units at almost right angles through a \(\mu_1\)-oxo bridge to each of the four individual phosphonate groups, whilst two axial aqua ligands (average bond length = 2.14 Å) complete the octahedral coordination sphere. Interestingly, there is a clear hydrogen bonding interaction between the benzoic acid moieties, whereby the clusters are organized into well-ordered 1D chain-like arrays with a mean distance of ca. 2.5 Å between the carboxylate moieties on each cluster unit. This suggests that the carboxylate groups on each POM remain protonated, providing one possible rationale for why no metal coordination takes place at these positions.

This result is especially noteworthy as we believe it is one of the very few examples of controllable post-functionalization of a hybrid-POM species with a heterometal group. In fact, the structure of 2 can be almost directly compared in a structural sense with the previously reported metal-bridged TMSP dimer species: \(\{\text{Zr}(P_2W_{17})_2\}\).\(^{14}\) Whilst we do note that this somewhat unexpected coordination mode has been observed previously in similar Keggin-type clusters,\(^{15}\) it has only been reported in cases where the POM core retains at least one vacant lacunary site with which to help coordinate additional transition metal species.

Whilst compound 3 is effectively isostructural to 2, compound 4 is instead linked into a dimeric species by a \((\text{Mn}_2(OH)_2)\)\(^2\) unit in which two \(\mu_2\)-hydroxo ions \((d_{\text{Mn-OH}} = 2.12 - 2.34 \text{ Å})\) bridge the Mn\(^{2+}\) centres between each POM subunit (Figure 1). As in the case of compounds 2 and 3, aqua ligands complete the coordination sphere of the cations, resulting in coordination environments with \(d_{\text{Mn-OH}} = 2.18\) and 2.21 Å for Mn1 and Mn2 respectively, consistent with their assignment as Mn\(^{2+}\) ions and correlating with bond valence sum calculations.\(^{16}\) As before, this structure can also be related to a previously reported \(\{\text{Zr}_2(P_2W_{17})_2\}\) TMSP dimer.\(^{14}\) In all cases, complimentary electrospray ionisation mass spectrometric (ESI-MS) analysis has been used to verify the identity of each cluster in tandem with additional spectroscopic analyses (including FT-IR and elemental analysis – see SI for additional details).

The cyclic voltammetry of compounds 2-4 was also studied as a comparison to that of compound 1. In all cases, small positive shifts of around 60 – 70 mV were observed between the half-wave potential of the first redox couple of the post-functionalised compounds versus the parent hybrid complex, indicating substantial modification of the LUMO energy of all
three metal-functionalised species. More significant positive shifts were observed on the subsequent redox processes, whereby the general trend is that of considerably more positive second and third redox half potentials (in the order of 200-300 and 400-500 mV respectively) in 2-4 relative to 1 (see Figure 2, Table 1 and SI). This clearly indicates that metal coordination at the bis-phosphonate site has a significant and direct effect on the redox properties of the POM. It is also important to note that in more commonly studied hybrid systems where metal cations have been coordinated to appended ligand groups (e.g. terpyridine), the electronic communication between the metal and the POM is generally so poor that the redox properties of the metal-oxide cluster are essentially unchanged.\(^\text{17}\) Here, the adoption of phosphonate ligands allows the electronic structure of the POM to be directly addressed by the addition of metals at the adventitiously formed bi-dentate bis-phosphonate coordination site.

Given that we have recently shown how modification of the redox potential of the POM core through hybridization with organophosphate moieties alone can also be used to both alter and selectively tune photo-activity,\(^\text{9,11}\) we were interested to see how metallation of the hybrid POM functionalised clusters are readily reduced by up to two electrons under visible light in the absence of oxygen. Data is shown at 2 minute intervals.

| Compound | E\(_{1/2}\) (1\(^{st}\)) / V | E\(_{1/2}\) (2\(^{nd}\)) / V | E\(_{1/2}\) (3\(^{rd}\)) / V |
|----------|------------------|------------------|------------------|
| 1        | 0.0              | -0.38            | -0.84            |
| 2        | 0.07             | -0.08            | -0.35            |
| 3        | 0.06             | -0.08            | -0.34            |
| 4        | 0.06             | -0.14            | -0.43            |

Table 1. Half-wave redox potentials observed for compounds 1-4 obtained by cyclic voltammetry (potentials referenced vs NHE).
transition-metal substitution approaches. The unexpected preference of secondary metal cations for coordination with the terminal oxygen groups on the bis-phosphonate moiety can be argued to represent an extension of the lacunary functionality of the parent [P_2W_{13}] anion, allowing the POM reactivity and electronic properties to be addressed directly whilst retaining the associated hybrid functionality of the appended ligand groups. For instance, the substantial positive shifts observed in the redox properties of the composite complexes 2-4 facilitate the 2e\(^{-}\) reduction of the POM under irradiation with high-energy visible light (\(\lambda > 390\) nm), a key requirement in next-generation materials for solar fuel production and other multi-electron catalytic processes. This potentially paves the way for the application of such species in new dyadic or triadic assemblies in which the tuneable electrochemical and photochemical properties of the POM can be combined with the near-limitless molecular design approaches available to hybrid-POM chemistry and the modular reactivity of transition-metal substituted POM species.

**Conflicts of interest**

The authors have no conflicts to declare.

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