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Insights into the coordination chemistry of phosphonate derivatives of heteropolyoxotungstates.

Richard Villanneau,^{*†} David Racimor,^{†,‡} Elisabeth Messner-Henning,[†] H el ene Rousseli ere,[†] S ebastien Picart,[‡] Ren e Thouvenot,^{*†} and Anna Proust^{†,§}

[†]Institut Parisien de Chimie Mol culaire, UMR CNRS 7201, UPMC Univ. Paris 6, Equipe Polyoxom tallates, Case courrier 42, 4 Place Jussieu, 75252 Paris cedex 05, France. [‡]CEA, DEN, DRCP, SCPS, LC2A, F-30207 Bagnols-sur-C ze, France. [§]Institut Universitaire de France, 103 B^d Saint-Michel, 75005 Paris, France. ^{*}Tel: + (33) 1 44 27 35 22. Fax: (+33) 1 44 27 38 41.

In memory of Dr. Marie-Madeleine Rohmer

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The coordination properties of vacant bis-phosphonate derivatives of polyoxometalates, with easily tunable functions, have been explored. Preparation and crystallographic structure of their La³⁺ and Zr⁴⁺ complexes are described herein.

Polyoxometalates (POMs) can provide polydentate coordination sites for most metal cations, including transition metal (TM) ions, among which lanthanides. Since POMs are π -donor and π -acceptor ligands at once, they are able to accommodate cations in a wide range of oxidation states. For example, Ru complexes of α -[PW₁₁O₃₉]⁷⁻ are known for Ru oxidation states ranging from +II to +VI.ⁱ Similarly rhenium may be incorporated in POM complexes as Re^V, Re^{VI} and Re^{VII},ⁱⁱ and both palladium and platinum cations in their +II and +IV oxidation states.^{iii,iv,v,vi} Regarding these unique properties, numerous TM derivatives of POMs have proven to be effective catalysts in various processes, in particular in oxidation reactions.^{vii} Recent reports include epoxidation of alkenes with H₂O₂ using various Ti⁴⁺ or Zr⁴⁺ derivatives of POMs,^{viii} and oxidation of water with ruthenium-incorporated heteropolyoxotungstates.^{ix,x} Examples of catalytic studies with lanthanides derivatives of POMs are scarce, but it has been recently shown that they can act as selective and recoverable Lewis acid catalysts.^{xi} Heterogenization of homogeneous processes by immobilization of TM POM derivatives onto oxide support can also be found in the literature. These studies generally involve either a simple physical adsorption of the catalyst^{xii} or an electrostatic interaction with a positively charged support, acting as a counter-ion.^{xiii} However, this kind of system is unavoidably subjected to partial loss of the active species during the catalytic process. Anchored homogeneous catalysts (AHCs), in which the catalyst is immobilized through a covalent bond onto a support, appear to be an elegant and efficient answer to the leaching of the catalyst, and would also improve its dispersion. Up to now, the use of hybrid

POMs for the preparation of AHCs has been barely explored.^{xiv} The principal reason lies in the difficulty to meet the requirements for such a system, *i. e.* functional arm(s) for grafting to the surface and coordination site(s) for welcoming the TM cations at once.

In the present work, we report on preliminary results on the coordination properties of the vacant bis-phosphonate [α -A-PW₉O₃₄{PO(R)}₂]⁵⁻,^{xv} in which R is an organic function that can be easily further derived. These species may potentially act as tetradentate ligands, and represent examples of the bi-functional organic-inorganic POMs hybrid we are looking for. They were prepared according to the classical phase-transfer synthesis of silane or phosphonate derivatives using tetraalkylammonium cations,^{xv,xvi} except for R = -CH₂CH₂COOH, for which the preparation has been adapted (see S1 in the SI).

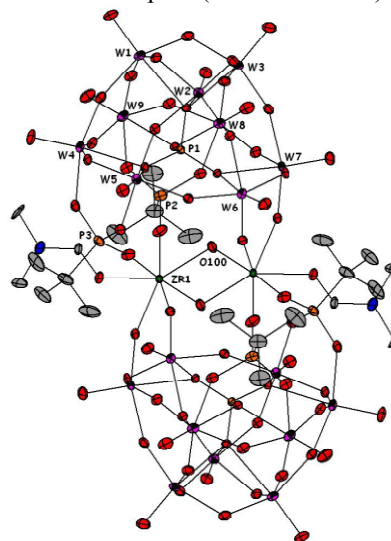


Figure 1: Molecular structure of the anion 1-*t*Bu-DMF. Ellipsoids for W, P and Zr are given at the 30 % probability level.^{xvii}

Reaction in refluxing acetonitrile for one night of (tBu₄N)₃Na₂[PW₉O₃₄{PO(R)}₂] (where R = *t*Bu, Ph, Et)

with 1.5 eq. of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ led to the formation of a unique species in the mother liquor as attested by its ^{31}P NMR spectrum. Slow evaporation of this solution in air allowed the formation of a white material, which has been identified as $(^{\text{t}}\text{Bu}_4\text{N})_4[\{\text{PW}_9\text{O}_{34}\{\text{PO}(\text{R})\}_2\}_2\{\text{Zr}(\text{H}_2\text{O})(\mu\text{-OH})\}_2] \cdot x\text{H}_2\text{O}$, $(^{\text{t}}\text{Bu}_4\text{N})_4\mathbf{1}\text{-R-H}_2\text{O} \cdot x\text{H}_2\text{O}$ (figure S4 (left) in the SI). Re-crystallization of these complexes in dimethylformamide (DMF) afforded crystals of $(^{\text{t}}\text{Bu}_4\text{N})_4[\{\text{PW}_9\text{O}_{34}\{\text{PO}(\text{R})\}_2\}_2\{\text{Zr}(\text{DMF})(\mu\text{-OH})\}_2]$, $(^{\text{t}}\text{Bu}_4\text{N})_4\mathbf{1}\text{-R-DMF}$, suitable for an X-ray diffraction study, in a moderate yield. The crystal structure has been resolved for both $\text{R} = ^{\text{t}}\text{Bu}$ (figure 1) and Ph (figure S4 (right) in the SI). The anion consists of two $[\text{PW}_9\text{O}_{34}\{\text{PO}(\text{R})\}_2]^{5-}$ units linked together by a $\{(\text{DMF})\text{Zr}(\text{OH})_2\text{-Zr}(\text{DMF})\}^{6+}$ bridge. The Zr^{4+} ion achieves a sevenfold coordination *via* the two free oxygen atoms of the lacuna of one $[\text{PW}_9\text{O}_{34}\{\text{PO}(\text{R})\}_2]^{5-}$ subunit and the two oxygen atoms of the phosphonate groups of the second unit. This bridging mode is different from that previously observed in other $\{\text{Zr}_2(\text{OH})_2\}^{6+}$ -containing POMs, *i.e.* $[\{\text{W}_5\text{O}_{18}\text{Zr}(\mu\text{-OH})\}_2]^{6-}$,^{xviii,xix} $[\{\text{PW}_{11}\text{O}_{39}\text{Zr}(\mu\text{-OH})\}_2]^{8-}$,^{viii} and $[\{\text{P}_2\text{W}_{17}\text{O}_{61}\text{Zr}(\mu\text{-OH})\}_2]^{14-}$.^{xx} Indeed, in all of them, the Zr^{4+} ion formally replaces a W^{6+} cation, and, consequently, is incorporated into the POM framework through coordination to five oxygen atoms of the same sub-unit.

Interestingly, some of these POMs have proved to be efficient catalysts in the epoxidation of alkenes with H_2O_2 .^{viii,xxi} Because of the presence of easily removable solvent molecules coordinated to Zr , $(^{\text{t}}\text{Bu}_4\text{N})_4\mathbf{1}\text{-R}$ compounds are interesting candidates for such catalytic applications, with the advantage of a possible modulation of the electronic and steric properties at the metal centers *via* the modification of the R group of the phosphonates.

Applying the previous procedure, but at room temperature, to $(^{\text{t}}\text{Bu}_4\text{N})_3\text{Na}_2[\text{PW}_9\text{O}_{34}\{\text{PO}(\text{tBu})\}_2]$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ led to the isolation of $(^{\text{t}}\text{Bu}_4\text{N})_2[\text{PW}_9\text{O}_{34}\{\text{PO}(\text{tBu})\}_2\{\text{La}(\text{DMF})_5(\text{H}_2\text{O})\}] \cdot 2\text{H}_2\text{O}$, $(^{\text{t}}\text{Bu}_4\text{N})_2\mathbf{2}\text{-tBu-DMF} \cdot 2\text{H}_2\text{O}$. X-ray diffraction study showed that the corresponding anion $\mathbf{2}\text{-tBu-DMF}$ consists of one La^{3+} ion coordinated to two oxygen atoms of $[\text{PW}_9\text{O}_{34}\{\text{PO}(\text{tBu})\}_2]^{5-}$, one water and five DMF molecules. It is noteworthy that among the four nucleophilic oxygen atoms, only those of the phosphonate groups are bound to the cation. The other oxygen atoms delimiting the lacuna (O_l) are involved in hydrogen bonding with the O_w atom of the water molecule linked to La^{3+} . The short ($\text{O}_l\text{-O}_w$) distances (2.71(1) Å) agree with strong stabilization energy in the molecule, as previously observed in other metallic derivatives of POMs.^{xxii}

Table 1 ^{31}P NMR chemical shifts of $(^{\text{t}}\text{Bu}_4\text{N})_3\text{Na}_2[\text{PW}_9\text{O}_{34}\{\text{PO}(\text{tBu})\}_2]$, $(^{\text{t}}\text{Bu}_4\text{N})_4\mathbf{1}\text{-Bu-H}_2\text{O}$, $(^{\text{t}}\text{Bu}_4\text{N})_4\mathbf{1}\text{-Bu-DMF}$ and $(^{\text{t}}\text{Bu}_4\text{N})_2\mathbf{2}\text{-Bu-DMF}$.

	$\{\text{PO}(\text{tBu})\}$	$\{\text{PO}_4\}$
$(^{\text{t}}\text{Bu}_4\text{N})_3\text{Na}_2[\text{PW}_9\text{O}_{34}\{\text{PO}(\text{tBu})\}_2]^{xxv}$	34.9	-11.4
	36.9*	-11.3*
$(^{\text{t}}\text{Bu}_4\text{N})_4\mathbf{1}\text{-tBu-H}_2\text{O}$	30.3*	-14.7*
$(^{\text{t}}\text{Bu}_4\text{N})_4\mathbf{1}\text{-tBu-DMF}$	30.6	-14.6
$(^{\text{t}}\text{Bu}_4\text{N})_2\mathbf{2}\text{-tBu-DMF}$	29.1	-14.2

Spectra obtained in $\text{DMF}/(\text{CD}_3)_2\text{CO}$ or in $\text{CH}_3\text{CN}/\text{CD}_3\text{CN}^*$

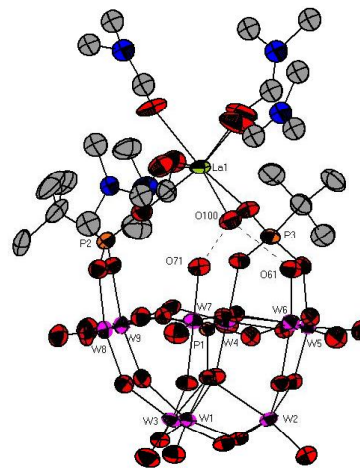


Figure 2. Molecular structure of the anion $\mathbf{2}\text{-tBu-DMF}$. Ellipsoids for W , P and La are given at the 50 % probability level. Dotted lines feature hydrogen bonds between the water molecule and $\text{O}(61)$ and $\text{O}(71)$.

The $\{^1\text{H}\}^{31}\text{P}$ NMR spectra of the two $^{\text{t}}\text{Bu}$ derivatives, $(^{\text{t}}\text{Bu}_4\text{N})_4\mathbf{1}\text{-tBu-DMF}$ and $(^{\text{t}}\text{Bu}_4\text{N})_2\mathbf{2}\text{-tBu-DMF}$, like that of the parent $(^{\text{t}}\text{Bu}_4\text{N})_3\text{Na}_2[\text{PW}_9\text{O}_{34}\{\text{PO}(\text{tBu})\}_2]$, display two peaks with relative intensity of 2:1. They have been respectively attributed to the P atoms of the phosphonate groups and of the central phosphate of $\{\text{PW}_9\text{O}_{34}\}$ core (see table 1). Both sets of resonances are displaced to lower chemical shifts with respect to the parent compound. The shift is more pronounced ($\Delta\delta \approx -5$ ppm) for $\{\text{PO}(\text{tBu})\}$, according to the Zr^{4+} or La^{3+} ions being directly coordinated to the phosphonate group. The shielding of the $\{\text{PO}_4\}$ signal was actually expected due to partial saturation of the vacancy.^{xv} Not surprisingly, this shift is significantly lower for anions $\mathbf{2}\text{-tBu}$, since the oxygen atoms of the lacuna are not directly involved in the coordination of the La^{3+} ion. In this case, the low frequency shift is probably due to the hydrogen bonds involving these oxygen atoms and the water molecule linked to La^{3+} .

The ^{183}W NMR spectra of all species consist of five lines with relative intensity 1/2/2/2/2, consistent with the C_{2h} or C_s symmetry of the anions $\mathbf{1}$ or $\mathbf{2}$ respectively. Two doublets are observed at -188.8 ($^2J_{\text{P-W}} \approx 8$ Hz) and -168.8 ppm ($^2J_{\text{P-W}} \approx 4$ Hz) for $\mathbf{1}\text{-tBu-DMF}$ and -192.7 ($^2J_{\text{P-W}} \approx 6$ Hz) and -181.8 ppm ($^2J_{\text{P-W}} \approx 8$ Hz) for $\mathbf{2}\text{-Ph-H}_2\text{O}$ respectively. These lines correspond to the tungsten atoms linked to the phosphonate groups. Comparison with the spectrum of the parent compound $(^{\text{t}}\text{Bu}_4\text{N})_3\text{Na}_2[\text{PW}_9\text{O}_{34}\{\text{PO}(\text{R})\}_2]$ is also instructive. Indeed, the spectra of $\mathbf{2}\text{-R-H}_2\text{O}$ ($\text{R} = \text{Ph}, ^{\text{t}}\text{Bu}$) are similar to those of their parent compounds, with a high frequency shift by *ca.* 10-15 ppm of all but $\text{W}(4) \equiv \text{W}(9)$ and $\text{W}(5) \equiv \text{W}(8)$ resonances (figures S5 and S6 in the SI). This observation is at variance with the behaviour of the Zr^{4+} derivative ($\mathbf{1}\text{-tBu-DMF}$); actually the lines assigned to the tungsten atoms $\text{W}(2) \equiv \text{W}(3)$ and $\text{W}(6) \equiv \text{W}(7)$, that are not linked to the phosphonate groups, are strongly displaced to low frequency (figure 2, table 2) due to the coordination of the Zr^{4+} ion.

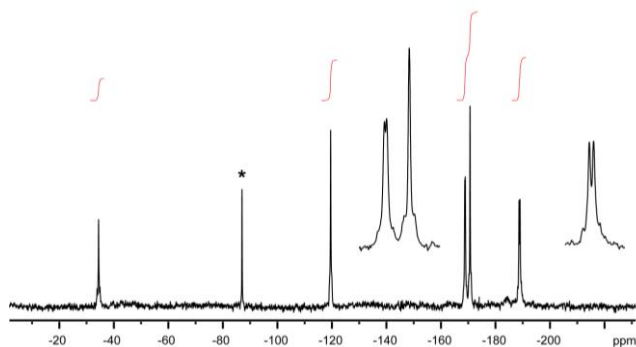


Figure 2: ^{183}W NMR spectrum of $(^t\text{Bu}_4\text{N})_4 1\text{-}^t\text{Bu-DMF}$ (0.415 g in 2.5 mL of DMF + 0.5 mL of CD_3COCD_3), with expansion of the low frequency signals showing the $^2J_{p-w}$ couplings. The spectrum has been recorded at 25.01 MHz in a 10 mm o.d. tube on a Bruker Avance 600 spectrometer equipped with a BBO probehead. The peak with a * is due to the presence of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ as an impurity.

Table 2 ^{183}W NMR chemical shifts of $(^t\text{Bu}_4\text{N})_3\text{Na}_2[\text{PW}_9\text{O}_{34}\{\text{PO}(^t\text{Bu})_2\}_2]$, $(^t\text{Bu}_4\text{N})_3\text{Na}_2[\text{PW}_9\text{O}_{34}\{\text{PO}(\text{Ph})_2\}_2]^{5-}$ and $(^t\text{Bu}_4\text{N})_4 1\text{-}^t\text{Bu-DMF}$ and $(^t\text{Bu}_4\text{N})_2 2\text{-Ph-H}_2\text{O}$.

	$[\text{PW}_9\text{O}_{34}\{\text{PO}(^t\text{Bu})_2\}_2]^{5-}$	$[\text{PW}_9\text{O}_{34}\{\text{PO}(\text{Ph})_2\}_2]^{5-}$	1- $^t\text{Bu-DMF}$	2-Ph-H ₂ O
W(1)	-44.2	-40.4	-34.4	-30.3
W(2)≡W(3)	-96.8	-92.5	} -119.5/-170.7 }	} -84.4/-126.7 }
W(6)≡W(7)	-141.6	-138.6		
W(4)≡W(9)	-180.0	-191.1	} -168.8/-188.8 }	} -181.8/-192.7 }
W(5)≡W(8)	-190.4	-192.9		

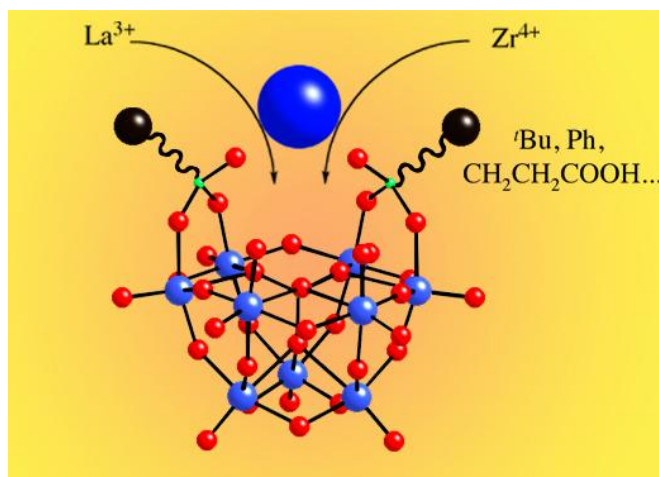
In conclusion, the results herein reported provide the first structural characterization by single crystal X-ray diffraction of phosphonate derivatives of trivalent heteropolyoxotungstates. Furthermore, we have shown that the $[\text{PW}_9\text{O}_{34}\{\text{PO}(\text{R})_2\}_2]^{5-}$ anions are still versatile ligands toward transition metal cations: they can act either as bidentate or bis-bidentate ligands. We have also shown that the complexation of cations does not depend on the nature (alkyl or aryl) of the organic arms of the phosphonate. This will allow further functionalization of POMs with useful organic functions whilst maintaining the complexation ability at the same time.

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Supporting Information Available: preparation of $(^t\text{Bu}_4\text{N})_3\text{Na}_2[\alpha\text{-A-PW}_9\text{O}_{34}\{\text{PO}(\text{CH}_2\text{CH}_2\text{COOH})_2\}_2]$; polyhedral representations of anions 1- $^t\text{Bu-H}_2\text{O}$ and 1-Ph-DMF; crystallographic data for $(^t\text{Bu}_4\text{N})_4 1\text{-Ph-DMF}$, $(^t\text{Bu}_4\text{N})_4 1\text{-}^t\text{Bu-DMF}\cdot 4\text{DMF}$, $(^t\text{Bu}_4\text{N})_4 1\text{-}^t\text{Bu-H}_2\text{O}\cdot 4\text{CH}_3\text{CN}$, and $(^t\text{Bu}_4\text{N})_2 2\text{-}^t\text{Bu-DMF}\cdot 2\text{H}_2\text{O}$; ^{183}W NMR spectra of $(^t\text{Bu}_4\text{N})_2 2\text{-Ph-H}_2\text{O}$ and $(^t\text{Bu}_4\text{N})_2 2\text{-}^t\text{Bu-H}_2\text{O}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

*To whom correspondence should be addressed. E-mail: richard.villanneau@upmc.fr. rene.thouvenot@upmc.fr.

Synopsis: The coordination properties of vacant bis-phosphonate derivatives of polyoxometalates with general formula $[PW_9O_{34}\{PO(R)\}_2]^{5-}$ have been explored. We have shown that these anions are versatile ligands toward transition metal cations since they can act either as bidentate or bis-bidentate ligands. Preparation, spectroscopic characterization and crystallographic structure of their La^{3+} and Zr^{4+} complexes are described. The presence of easily tunable phosphonate functions makes them attractive candidates for further functionalization of POMs with useful organic functions.



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radiation (λ 0.71073 Å), θ range = 2.53 to 30.0 °, 29073 unique of 83239 reflections collected. A total of 979 parameters were used for the full-matrix least-squares refinement of F_2 , $R_{\text{int}}=0.0607$, $R_1=0.0589$ [$I > 2\sigma(I)$], $R_1=0.0924$ (all data); $wR_2 = 0.1485$ [$I > 2\sigma(I)$], $wR_2 = 0.1653$ (all data). Further details are given in the Supporting Information. CCDC 785548 to 785551 contain the supplementary crystallographic data for this paper. The atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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