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Insights into the Coordination Chemistry of Phosphonate Derivatives of Heteropolyoxotungstates[†]

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The coordination properties of vacant bisphosphonate derivatives of polyoxometalates, with easily tunable functions, have been explored. The preparation and crystallographic structure of their La^{3+} and Zr^{4+} complexes are described herein.

Polyoxometalates (POMs) can provide polydentate coordination sites for most metal cations, including transition-metal (TM) ions, among which are lanthanides. Because POMs are π-donor and -acceptor ligands at the same time, they are able to accommodate cations in a wide range of oxidation states. For example, Ru complexes of α-$[PW_{11}O_{39}]^{7-}$ are known for oxidation states ranging from II to VI.[1] Similarly, Re may be incorporated into POM complexes as Re$^{\mathrm{V}}$, Re$^{\mathrm{VI}}$, and Re$^{\mathrm{VII}}$[2] and both Pd and Pt cations in their II and IV oxidation states.[3−6] Regarding these unique properties, numerous TM derivatives of POMs have proven to be effective catalysts in various processes, in particular in oxidation reactions.[7] Recent reports include the epoxidation of alkenes with H_2O_2 using various Ti^{4+} or Zr^{4+} derivatives of POMs,[8] and the oxidation of water with Ru-incorporated heteropolyoxotungstates.[9,10] Examples of catalytic studies with lanthanide derivatives of POMs are scarce, but it has been recently shown that they can act as selective and recoverable Lewis acid catalysts.[11] Heterogenization of homogeneous processes by immobilization of TM POM derivatives onto oxide supports can also be found in the literature. These studies generally involve either a simple physical adsorption of the catalyst[12] or an electrostatic interaction with a positively charged support, acting as a counterion.[13] However, this kind of system is

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[†] In memory of Dr. Marie-Madeleine Rohmer.

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(1) (a) Rong, C.; Pope, M. T. *J. Am. Chem. Soc.* **1992**, *114*, 2932–2938. (b) Lahootun, V.; Besson, C.; Villanneau, R.; Villain, F.; Chamoreau, L.-M.; Boubekeur, K.; Blanchard, S.; Thouvenot, R.; Proust, A. *J. Am. Chem. Soc.* **2007**, *129*, 7127–7135.

(2) (a) Ortega, F.; Pope, M. T.; Evans, R. H. T., Jr. *Inorg. Chem.* **1997**, *36*, 2166–2169. (b) Kwen, H.; Tomlinson, S.; Maatta, E. A.; Dablemont, C.; Thouvenot, R.; Proust, A.; Gouzerh, P. *Chem. Commun* **2002**, 2970–2971.

(3) (a) Anderson, T. M.; Cao, R.; Slonkina, E.; Hedman, B.; Hodgson, K. O.; Hardcastle, K. I.; Neiwert, W. A.; Wu, S.; Kirk, M. L.; Knottenbelt, S.; Depperman, E. C.; Keita, B.; Nadjo, L.; Musaev, D. G.; Morokuma, K.; Hill, C. L. *J. Am. Chem. Soc.* **2005**, *127*, 11948–11949. (b) Anderson, T. M.; Neiwert, W. A.; Kirk, M. L.; Piccoli, P. M. B.; Schultz, A. J.; Koetzle, T. F.; Musaev, D. G.; Morokuma, K.; Cao, R.; Hill, C. L. *Science* **2004**, *306*, 2074–2077.

(4) (a) Bi, L. H.; Reicke, M.; Kortz, U.; Keita, B.; Nadjo, L.; Clark, R. J. *Inorg. Chem.* **2004**, *43*, 3915–3920. (b) Bi, L. H.; Kortz, U.; Keita, B.; Nadjo, L.; Daniels, L. *Eur. J. Inorg. Chem.* **2005**, 3034–3041. (c) Lee, U.; Joo, H.-C.; Park, K.-M.; Mal, S. S.; Kortz, U.; Keita, B.; Nadjo, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 793–796.

(5) Villanneau, R.; Renaudineau, S.; Herson, P.; Boubekeur, K.; Thouvenot, R.; Proust, A. *Eur. J. Inorg. Chem.* **2009**, 479–488.

(6) (a) Angus-Dunne, S.; Burns, R. C.; Craig, D. C.; Lawrance, G. A. *Z. Anorg. Allg. Chem.* **2010**, *636*, 727–734. (b) Lee, U.; Joo, H.-C. *Acta Crystallogr.* **2004**, *E60*, i86–i88.

(7) (a) Kozhevnikov, I. V. *Catalysis by Polyoxometalates*; Wiley: Chichester, England, 2002. (b) Mizuno, N.; Yamaguchi, K.; Kanata, K. *Coord. Chem. Rev.* **2005**, *249*, 1944–1956. (c) Hill, C. L.; Delannoy, L.; Duncan, D. C.; Weinstock, I. A.; Renneke, R. F.; Reiner, R. S.; Atalla, R. H.; Han, J. W.; Hillesheim, D. A.; Cao, R.; Anderson, T. M.; Okun, N. M.; Musaev, D. G.; Geletii, Y. V. *C. R. Chim.* **2007**, *10*, 305–312. (d) Topical issue on POMs in catalysis: Hill, C. L., guest editor. *J. Mol. Catal. A: Chem.* **2007**, *262*, 1−242. (e) Neumann, R. *Inorg. Chem.* **2010**, *49*, 3594–3601.

(8) (a) Kholdeeva, O. A.; Maksimov, G. M.; Maksimovskaya, R. I.; Vanina, M. P.; Trubitsina, T. A.; Naumov, D. Y.; Kolesov, B. A.; Antonova, N. S.; Carbo, J. J.; Poblet, J. M. *Inorg. Chem.* **2006**, *45*, 7224–7234. (b) Kholdeeva, O. A. *Top. Catal.* **2006**, *40*, 229–243. (c) Antonova, N. S.; Carbo, J. J.; Kortz, U.; Kholdeeva, O. A.; Poblet, J. M. *J. Am. Chem. Soc.* **2010**, *132*, 7488–7497.

(9) (a) Geletii, Y. V.; Botar, B.; Kögerler, P.; Hillesheim, D. A.; Musaev, D. G.; Hill, C. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 3896–3899. (b) Besson, C.; Huang, Z.; Geletii, Y. V.; Lense, S.; Hardcastle, K. I.; Musaev, D. G.; Lian, T.; Proust, A.; Hill, C. L. *Chem. Commun.* **2010**, 2784–2786.

(10) (a) Sartorel, A.; Carraro, M.; Scorrano, G.; De Zorzi, R.; Geremia, S.; McDaniel, N. D.; Bernhard, S.; Bonchio, M. *J. Am. Chem. Soc.* **2008**, *130*, 5006–5007. (b) Puntoriero, F.; La Ganga, G.; Sartorel, A.; Carraro, M.; Scorrano, G.; Bonchio, M.; Campagna, S. *Chem. Commun.* **2010**, 4725–4727.

(11) Boglio, C.; Lemière, G.; Hasenknopf, B.; Thorimbert, S.; Lacote, E.; Malacria, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3324–3327.

(12) Okuhara, T.; Mizuno, N.; Misono, M. *Adv. Catal.* **1996**, *41*, 113–252.

(13) (a) Okun, N. M.; Ritorto, M. D.; Anderson, T. M.; Apkarian, R. P.; Hill, C. L. *Chem. Mater.* **2004**, *16*, 2551–2558. (b) Vazylyev, M.; Sloboda-Rozner, D.; Haimov, A.; Maayan, G.; Neumann, R. *Top. Catal.* **2005**, *34*, 93–99. (c) Chen, L; Zhu, K.; Bi, L.-H.; Suchopar, A.; Reicke, M.; Mathys, G.; Jaensch, H.; Kortz, U.; Richards, R. M. *Inorg. Chem.* **2007**, *46*, 8457–8459.

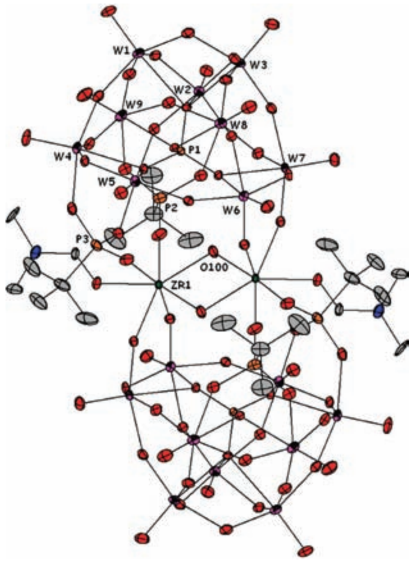

Figure 1. Molecular structure of the anion **1-^{t}Bu-DMF**. Ellipsoids for W, P, and Zr are given at the 30% probability level.[17].

unavoidably subjected to a 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 barely been explored.[14] The principal reason lies in the difficulty of meeting 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 the same time.

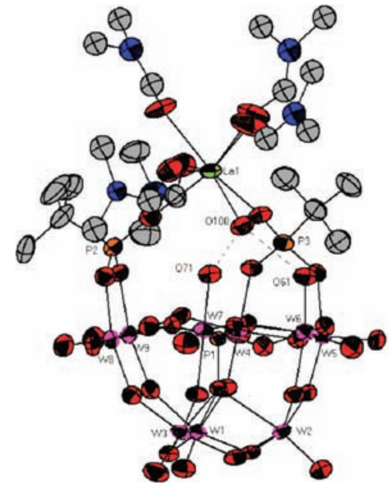

Figure 2. Molecular structure of the anion **2-^{t}Bu-DMF**. Ellipsoids for W, P, and La are given at the 50% probability level. Dotted lines feature hydrogen bonds between the water molecule and O61 and O71.

In the present work, we report on preliminary results on the coordination properties of the vacant bisphosphonate $[\alpha\text{-A-PW}_9O_{34}\{PO(R)\}_2]^{5-}$,[15] in which R is an organic function that can easily be further derived. These species may potentially act as tetradentate ligands and represent examples of the bifunctional organic−inorganic POM hybrid that we are looking for. They were prepared according to the classical phase-transfer synthesis of silane or phosphonate derivatives using tetraalkylammonium cations,[15,16] except for R = $-CH_2CH_2COOH$, for which the preparation has been adapted (see S1 in the Supporting Information, SI).

The reaction of $(^n\text{Bu}_4\text{N})_3\text{Na}_2[\text{PW}_9\text{O}_{34}\{\text{PO(R)}\}_2]$ (where R = ^{t}Bu, Ph, Et) with 1.5 equiv of $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ in refluxing acetonitrile for 1 night 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 for the formation of a white material, which has been identified as $(^n\text{Bu}_4\text{N})_4[\{\text{PW}_9\text{O}_{34}\{\text{PO(R)}\}_2\}_2\{\text{Zr(H}_2\text{O)}(\mu\text{-OH})\}_2]\cdot x\text{H}_2\text{O}$ [$(^n\text{Bu}_4\text{N})_4$**1-R-H$_2$O**$\cdot x\text{H}_2\text{O}$; Figure S4 (left) in the SI]. Recrystallization of these complexes in dimethylformamide (DMF) afforded crystals of $(^n\text{Bu}_4\text{N})_4[\{\text{PW}_9\text{O}_{34}\{\text{PO(R)}\}_2\}_2\{\text{Zr(DMF)}(\mu\text{-OH})\}_2]$ [$(^n\text{Bu}_4\text{N})_4$**1-R-DMF**] suitable for an X-ray diffraction study, in moderate yield. The crystal structures have been resolved for both R = ^{t}Bu (Figure 1) and Ph [Figure S4 (right) in the SI]. The anion consists of two $[\text{PW}_9\text{O}_{34}\{\text{PO(R)}\}_2]^{5-}$ units linked together by a $\{(\text{DMF})\text{Zr(OH)}_2\text{-Zr(DMF)}\}^{6+}$ bridge. The Zr^{4+} ion achieves 7-fold coordination via the two free O atoms of the lacuna of one $[\text{PW}_9\text{O}_{34}\{\text{PO(R)}\}_2]^{5-}$ subunit and the two O 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., $[\{\text{W}_5\text{O}_{18}\text{Zr}(\mu\text{-OH})\}_2]^{6-}$,[18,19] $[\{\text{PW}_{11}\text{O}_{39}\text{Zr}(\mu\text{-OH})\}_2]^{8-}$,[8] and $[\{\text{P}_2\text{W}_{17}\text{O}_{61}\text{Zr}(\mu\text{-OH})\}_2]^{14-}$.[20] Indeed, in all of them, the Zr^{4+} ion formally replaces a W^{6+} cation and, consequently, is incorporated into the POM

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(14) (a) Schroden, R. C.; Blanford, C. F.; Melde, B. J.; Johnson, B. J. S.; Stein, A. *Chem. Mater.* **2001**, *13*, 1074–1081. (b) Zhang, R.; Yang, C. *J. Mater. Chem.* **2008**, *18*, 2691–2703.

(15) Mayer, C. R.; Thouvenot, R. *J. Chem. Soc., Dalton Trans.* **1998**, 7–13.

(16) (a) Kim, G.-S.; Hagen, K. S.; Hill, C. L. *Inorg. Chem.* **1992**, *31*, 5316–5324. (b) Mayer, C. R.; Herson, P.; Thouvenot, R. *Inorg. Chem.* **1999**, *38*, 6152–6158. (c) Racimor, D. Ph.D. Thesis, UPMC Paris 6, 2003. (d) Proust, A.; Thouvenot, R.; Gouzerh, P. *Chem. Commun.* **2008**, 1837–1852.

(17) For $(^n\text{Bu}_4\text{N})_4$**1-^{t}Bu-DMF·3DMF**. Anal. Calcd for $\text{C}_{95}\text{H}_{217}\text{N}_9\text{O}_{79}\text{P}_6\text{W}_{18}\text{Zr}_2$: C, 17.75; H, 3.40; N, 1.96. Found: C, 17.57; H, 3.31; N, 1.93. Crystals of $(^n\text{Bu}_4\text{N})_4$**1-^{t}Bu-DMF·4DMF**: M_r = 6500.43, crystal dimensions (mm^3) 0.6 × 0.2 × 0. 1, monoclinic, space group $P2_1/n$, a = 15.162(4) Å, b = 27.858(5) Å, c = 20.453(3) Å, β = 93.381(10)°, V = 8624(3) Å^3, Z = 2, D_{calc} = 2.503 Mg m^{-3}, μ = 12.204 mm^{-1}, T = 200 K, Mo Kα radiation (λ = 0.710 73 Å), θ range = 2.58−30.0°, 25 028 unique of 89 997 reflections collected. A total of 1022 parameters were used for the full-matrix least-squares refinement of F^2, R_{int} = 0.0656, R1 = 0.0379 [$I > 2\sigma(I)$] and 0.0722 (all data), and wR2 = 0.0738 [$I > 2\sigma(I)$] and 0.0832 (all data). For $(^n\text{Bu}_4\text{N})_2$**2-^{t}Bu-DMF·2H$_2$O**. Anal. Calcd for $\text{C}_{55}\text{H}_{131}\text{La}_1\text{N}_7\text{O}_{44}\text{P}_3\text{W}_9$: C, 18.98; H, 3.79; N, 2.82. Found: C, 18.85; H, 3.92; N, 2.73. Crystals of $(^n\text{Bu}_4\text{N})_2$**2-^{t}Bu-DMF·2H$_2$O**: M_r = 6962.28, crystal dimensions (mm^3) 0.5 × 0.45 × 0.25, triclinic, space group $P\bar{1}$, a = 14.233(2) Å, b = 16.884(2) Å, c = 22.433(3) Å, α = 90.792(11)°, β = 97.239(13)°, γ = 107.305(12)°, V = 5098(1) Å^3, Z = 1, D_{calc} = 2.268 Mg m^{-3}, μ = 10.643 mm^{-1}, T = 200 K, Mo Kα radiation (λ = 0.710 73 Å), θ range = 2.53−30.0°, 29 073 unique of 83 239 reflections collected. A total of 979 parameters were used for the full-matrix least-squares refinement of F^2, R_{int} = 0.0607, R1 = 0.0589 [$I > 2\sigma(I)$] and 0.0924 (all data), and wR2 = 0.1485 [$I > 2\sigma(I)$] and 0.1653 (all data). Further details are given in the SI. CCDC 785548−785551 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.

(18) Carabineiro, H.; Villanneau, R.; Carrier, X.; Herson, P.; Lemos, F.; Ribeiro, F. R.; Proust, A.; Che, M. *Inorg. Chem.* **2006**, *45*, 1915–1923.

(19) Errington, R. J.; Petkar, S. S.; Middleton, P. S.; McFarlane, W.; Clegg, W.; Coxall, R. A.; Harrington, R. W. *J. Am. Chem. Soc.* **2007**, *129*, 12181–12196.

(20) Sokolov, M. N.; Izarova, N. V.; Peresypkina, E. V.; Virovets, A. V.; Fedin, V. P. *Russ. Chem. Bull. Int. Ed.* **2009**, *58*, 507–512.

Table 1. ^{31}P NMR Chemical Shifts of $(^n\mathrm{Bu_4N})_3\mathrm{Na_2[PW_9O_{34}\{PO(^tBu)\}_2]}$, $(^n\mathrm{Bu_4N})_4$**1-^{t}Bu-H$_2$O**, $(^n\mathrm{Bu_4N})_4$**1-^{t}Bu-DMF**, and $(^n\mathrm{Bu_4N})_2$**2-^{t}Bu-DMF** in DMF/$(\mathrm{CD_3})_2\mathrm{CO}$

	$\{\mathrm{PO(^tBu)}\}$	$\{\mathrm{PO_4}\}$
$(^n\mathrm{Bu_4N})_3\mathrm{Na_2[PW_9O_{34}\{PO(^tBu)\}_2]}$[15]	34.9	−11.4
	36.9[a]	−11.3[a]
$(^n\mathrm{Bu_4N})_4$**1-^{t}Bu-H$_2$O**	30.3[a]	−14.7[a]
$(^n\mathrm{Bu_4N})_4$**1-^{t}Bu-DMF**	30.6	−14.6
$(^n\mathrm{Bu_4N})_2$**2-^{t}Bu-DMF**	29.1	−14.2

[a] Spectra obtained in $\mathrm{CH_3CN/CD_3CN}$.

framework through coordination to five O atoms of the same subunit.

Interestingly, some of these POMs have proven to be efficient catalysts in the epoxidation of alkenes with $\mathrm{H_2O_2}$.[8,21] Because of the presence of easily removable solvent molecules coordinated to Zr, $(^n\mathrm{Bu_4N})_4$**1-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 modification of the R group of the phosphonates.

Applying the previous procedure, but at room temperature, to $(^n\mathrm{Bu_4N})_3\mathrm{Na_2[PW_9O_{34}\{PO(^tBu)\}_2]}$ and $\mathrm{La(NO_3)_3\cdot 6H_2O}$ led to the isolation of $(^n\mathrm{Bu_4N})_2\mathrm{[PW_9O_{34}\{PO(^tBu)\}_2\{La(DMF)_5(H_2O)\}]\cdot 2H_2O}$, $(^n\mathrm{Bu_4N})_2$**2-^{t}Bu-DMF**$\cdot 2\mathrm{H_2O}$. An X-ray diffraction study (Figure 2) showed that the corresponding anion **2-^{t}Bu-DMF** consists of one $\mathrm{La^{3+}}$ ion coordinated to two O atoms of $\mathrm{[PW_9O_{34}\{PO(^tBu)\}_2]^{5-}}$, one water, and five DMF molecules. It is noteworthy that, among the four nucleophilic O atoms, only those of the phosphonate groups are bound to the cation. The other O atoms delimiting the lacuna ($\mathrm{O_l}$) are involved in hydrogen bonding with the $\mathrm{O_w}$ atom of the water molecule linked to $\mathrm{La^{3+}}$. The short ($\mathrm{O_l-O_w}$) distances [2.71(1) Å] agree with the strong stabilization energy in the molecule, as was previously observed in other metallic derivatives of POMs.[22]

The $\{^1\mathrm{H}\}^{31}\mathrm{P}$ NMR spectra of the two ^{t}Bu derivatives, $(^n\mathrm{Bu_4N})_4$**1-^{t}Bu-DMF** and $(^n\mathrm{Bu_4N})_2$**2-^{t}Bu-DMF**, like that of the parent $(^n\mathrm{Bu_4N})_3\mathrm{Na_2[PW_9O_{34}\{PO(^tBu)\}_2]}$, display two peaks with a relative intensity of 2:1. They have been respectively attributed to the P atoms of the phosphonate groups and of the central phosphate of $\{\mathrm{PW_9O_{34}}\}$ 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 $\{\underline{\mathrm{P}}\mathrm{O(^tBu)}\}$, due to the $\mathrm{Zr^{4+}}$ or $\mathrm{La^{3+}}$ ions being directly coordinated to the phosphonate group. The shielding of the $\{\mathrm{PO_4}\}$ signal was actually expected because of partial saturation of the vacancy.[15] Not surprisingly, this shift is significantly lower for anions **2-^{t}Bu** because the O atoms of the lacuna are not directly involved in coordination of the $\mathrm{La^{3+}}$ ion. In this case, the low-frequency shift is probably due to the hydrogen bonds involving these O atoms and the water molecule linked to $\mathrm{La^{3+}}$.

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 **1** or **2**, respectively. Two doublets are observed at −188.8 ($^2J_{\mathrm{P-W}} \approx 8$ Hz) and −168.8 ppm ($^2J_{\mathrm{P-W}} \approx 4$ Hz) for **1-^{t}Bu-DMF** and −192.7 ($^2J_{\mathrm{P-W}} \approx 6$ Hz) and −181.8 ppm ($^2J_{\mathrm{P-W}} \approx 8$ Hz) for **2-Ph-H$_2$O**. These lines correspond to the W atoms linked to the phosphonate groups. A comparison with the spectrum of the parent compound $(^n\mathrm{Bu_4N})_3\mathrm{Na_2[PW_9O_{34}\{PO(R)\}_2]}$ is also instructive. Indeed, the spectra of **2-R-H$_2$O** (R = Ph, ^{t}Bu) are similar to those of their parent compounds, with a high-frequency shift by ca. 10−15 ppm of all but W4≡W9 and W5≡W8 resonances (Figures S5 and S6 in the SI). This observation is at variance with the behavior of the $\mathrm{Zr^{4+}}$ derivative (**1-^{t}Bu-DMF**); actually, the lines assigned to the W atoms W2≡W3 and W6≡W7, which are not linked to the phosphonate groups, are strongly displaced to low frequency (Figure 3 and Table 2) because of coordination of the $\mathrm{Zr^{4+}}$ ion.

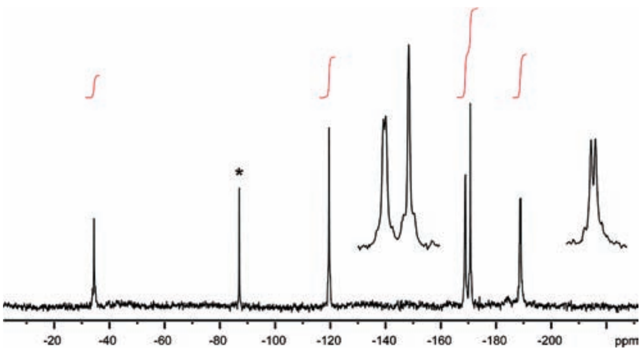

Figure 3. ^{183}W NMR spectrum of $(^n\mathrm{Bu_4N})_4$**1-^{t}Bu-DMF** (0.415 g in 2.5 mL of DMF + 0.5 mL of $\mathrm{CD_3COCD_3}$), with expansion of the low-frequency signals showing the $^2J_{\mathrm{P-W}}$ couplings. The spectrum has been recorded at 25.01 MHz in a 10-mm-o.d. tube on a Bruker Avance 600 spectrometer equipped with a BBO probehead. The peak indicated with an asterisk is due to the presence of $\mathrm{[PW_{12}O_{40}]^{3-}}$ as an impurity.

Table 2. ^{183}W NMR Chemical Shifts of $(^n\mathrm{Bu_4N})_3\mathrm{Na_2[PW_9O_{34}\{PO(^tBu)\}_2]}$, $(^n\mathrm{Bu_4N})_3\mathrm{Na_2[PW_9O_{34}\{PO(Ph)\}_2]}$,[15] $(^n\mathrm{Bu_4N})_4$**1-^{t}Bu-DMF**, and $(^n\mathrm{Bu_4N})_2$**2-Ph-H$_2$O**

	$\mathrm{[PW_9O_{34}\text{-}\{PO(^tBu)\}_2]^{5-}}$	$\mathrm{[PW_9O_{34}\text{-}\{PO(Ph)\}_2]^{5-}}$	1-^{t}Bu-DMF	2-Ph-H$_2$O
W1	−44.2	−40.4	−34.4	−30.3
W2≡W3	−96.8	−92.5	−119.5/−170.7	−84.4/−126.7
W6≡W7	−141.6	−138.6		
W4≡W9	−180.0	−191.1	−168.8/−188.8	−181.8/−192.7
W5≡W8	−190.4	−192.9		

In conclusion, the results herein reported provide the first structural characterization of phosphonate derivatives of trivacant heteropolyoxotungstates by single-crystal X-ray diffraction. Furthermore, we have shown that the $\mathrm{[PW_9O_{34}\{PO(R)\}_2]^{5-}}$ anions are still versatile ligands toward TM cations: they can act either as bidentate or bis-bidentate ligands. We have also shown that complexation of the 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, while maintaining the complexation ability at the same time.

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Supporting Information Available: X-ray crystallographic data in CIF format, preparation of $(^n\mathrm{Bu_4N})_3\mathrm{Na_2[\alpha\text{-}A\text{-}PW_9O_{34}\{PO(CH_2CH_2COOH)\}_2]}$, polyhedral representations of anions 1-^{t}Bu-H$_2$O and 1-Ph-DMF, crystallographic data for $(^n\mathrm{Bu_4N})_4$1-Ph-DMF, $(^n\mathrm{Bu_4N})_4$1-^{t}Bu-DMF$\cdot$4DMF, $(^n\mathrm{Bu_4N})_4$1-^{t}Bu-H$_2$O$\cdot$4CH$_3$CN, and $(^n\mathrm{Bu_4N})_2$2-^{t}Bu-DMF$\cdot$2H$_2$O, ^{183}W NMR spectra of $(^n\mathrm{Bu_4N})_2$2-Ph-H$_2$O and $(^n\mathrm{Bu_4N})_2$2-^{t}Bu-H$_2$O. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Poizat, M. Villanneau, R. Launay, F. Proust, A. Unpublished results.

(22) Laurencin, D.; Villanneau, R.; Gérard, H.; Proust, A. *J. Phys. Chem. A* **2006**, *110*, 6345–6355.