

Electronic Properties and Stability of Ditunganium^{IV} Substituted α -Keggin Polyoxotungstate with Heteroatom Phosphorus by DFT

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The electronic properties, redox properties, protonation, and stability of five $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ isomers have been investigated employing density-functional theory (DFT) method. The results reveal that the stability of $[\alpha\text{-1,2-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ and $[\alpha\text{-1,6-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ is weaker and the redox ability is higher among five isomers, while for $[\alpha\text{-1,5-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$, $[\alpha\text{-1,4-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$, and $[\alpha\text{-1,11-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ the stability is higher, but the redox ability is weaker. At the same time, Ti-substituted systems are preferentially reduced in the tungsten centers. A simple analysis of molecular electrostatic potential maps of $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ isomers suggests that the preferred protonation site corresponds to bridging oxygens (OTi₂ and OTiW) and terminal oxygens (OTi), especially bridging oxygens bonded to titaniums (OTi₂) in $[\alpha\text{-1,2-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ and $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$. It is proposed that the most stable structure is formed preferentially after protonation of the Ti–O site from the study of the protonated species, $[\alpha\text{-1,4-HPTi}_2\text{W}_{10}\text{O}_{40}]^{6-}$. By means of total bonding energies of $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ isomers, the relative sequence of stability has then been shown to be $[\alpha\text{-1,4-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-} > [\alpha\text{-1,5-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-} > [\alpha\text{-1,11-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-} > [\alpha\text{-1,2-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-} > [\alpha\text{-1,6-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$. In addition, the one-electron-reduced species of $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ are also discussed.

Introduction

The Keggin-type¹ heteropolyanions are important materials that promise a broad range of potential applications. Their excellent properties related to functional materials, such as catalysis, magnetism, and medicine, have been quite attractive.² The electronic properties and magnetism have also been studied theoretically.^{3,4} In particular, the polyoxotungstates substituted by lower oxidation state transition metal ions, such as vanadium(V), niobium(V), or titanium(IV), have been intensively studied, because their electronic properties and magnetism can be modified remarkably and they allow

covalent bonding of organometallic fragments to specific binding sites on the polyoxoanion surface.⁵

Among the various polyoxoanions, di-Ti-substituted Keggin structure $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ isomers are of particular interest, exhibit high catalytic activity, and have been proven to inhibit the replication of several enveloped DNA and RNA viruses.⁶

The structure of $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ was first proposed by Knoth using ¹⁸³W NMR spectroscopy in 1983;⁷ subsequently, Domaille concluded that $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ isomers had five

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(1) Keggin, J. F. *Nature* **1933**, *131*, 908.
(2) (a) Baker, L. C. W.; Figgis, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 3794.
(b) Pope, M. L.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34. (c) Yamase, T. *J. Chem. Soc., Dalton Trans.* **1991**, 3055. (d) Hill, C. L.; Prosser-McCartha, C. M. *Coord. Chem. Rev.* **1995**, *143*, 407. (e) Okuhara, T.; Mizuno, N.; Misono, M. *Adv. Catal.* **1996**, *41*, 113. (f) Hill, C. L., Ed. *Chem. Rev.* **1998**, *98*, 1. (g) Baker, L. C. W.; Glick, D. C. *Chem. Rev.* **1998**, *98*, 3. (h) Neumann, R. *Prog. Inorg. Chem.* **1998**, *47*, 317. (i) Zeng, H.; Newkome, G. R.; Hill, C. T. *Angew. Chem., Int. Ed.* **2000**, *39*, 1771. (j) Pope, M., Müller, A., Eds. *Polyoxometalate Chemistry from Topology via Self-Assembly to Applications*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001.

(3) (a) Maestre, J. M.; Poblet, J. M.; Bo, C.; Pastor, N. C.; Romero, P. G. *Inorg. Chem.* **1998**, *37*, 3444. (b) López, X.; Maestre, J. M.; Bo, C.; Poblet, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 9571. (c) Maestre, J. M.; López, X.; Bo, C.; Poblet, J. M. *Inorg. Chem.* **2002**, *41*, 1883. (d) Poblet, J. M.; López, X.; Bo, C. *Chem. Soc. Rev.* **2003**, *32*, 297. (e) Bridgeman, A. J.; Cavigliasso, G. *J. Chem. Soc., Dalton Trans.* **2002**, 2244. (f) Bridgeman, A. J.; Cavigliasso, G. *J. Phys. Chem. A* **2003**, *107*, 6613.
(4) (a) Maestre, J. M.; López, X.; Bo, C.; Poblet, J. M.; Casañ-Pastor, N. *J. Am. Chem. Soc.* **2001**, *123*, 3749. (b) López, X.; Bo, C.; Poblet, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 12574. (c) Bridgeman, A. J.; Cavigliasso, G. *Inorg. Chem.* **2002**, *41*, 1761. (d) Bridgeman, A. J.; Cavigliasso, G. *Inorg. Chem.* **2002**, *41*, 3500. (e) Kholdeeva, O. A.; Trubitsina, T. A.; Maksimovskaya, R. I.; Golovin, A. V.; Neiwert, W. A.; Kolesov, B. A.; López, X.; Poblet, J. M. *Inorg. Chem.* **2004**, *43*, 2284.

symmetries: C_1 , C_2 , C_{2v} , and two symmetric C_s .⁸ In 1991, the structures were confirmed by X-ray crystallography.⁹ However, up to now only the anion with C_2 symmetry had been obtained through experiment. According to those structural determinations, each $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ isomer usually exists as a monomer wherever in solution or in the solid state, while the dimeric, Ti–O–Ti bridged anhydride form of the di-Ti-substituted α -Keggin polyoxotungstate, $[\alpha\text{-1,6-PTi}_2\text{W}_{10}\text{O}_{40}]^{10-}$, has been reported.¹⁰ The reason for this phenomena needs to be explained and then needs to direct further experiments. Also, this explanation can help people to realize the structure of other di-Ti-substituted polyoxometalate (POMs), such as $[\text{SiTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$ or $[\text{CoTi}_2\text{W}_{10}\text{O}_{40}]^{9-}$. However, although theoretical studies on electric properties and structural stability of polyoxometalates are obviously lacking at present, we have achieved the first investigations of electronic properties, redox properties, protonation, and stability on the α -Keggin anions mentioned in the title using DFT method.

Computational Details

The DFT calculations were carried out using the ADF2003.01¹¹ suite of programs. The local density approximation (LDA) characterized by the functional of Vosko–Wilk–Nusair (VWN)¹²

parametrization is adopted for correlation functional. In addition, gradients corrections of Beck¹³ and Perdew¹⁴ (BP86) nonlocal corrections are employed for the exchange and correlation functionals, respectively. The valence atomic orbitals of titanium, phosphorus, oxygen, and hydrogen atoms were described by triple- ζ plus polarization Slater basis sets (ADF database TZP). A frozen core composed of 1s to 4spd shells for tungsten was described by means of single Slater functions (ADF W.4d type TZP). Due to the variational instability of the Pauli Hamiltonian,¹⁵ the quasi-relativistic Pauli method can only be applied with the frozen core approximation. The zero order regular approximation (ZORA)¹⁶ is variationally stable and can be used in all-electron calculations. So with the same density functionals, the calculations were first computed only based on the TZP basis set and then through adding the ZORA method to it. Spin-restricted calculations were performed on six ground-state structures, whereas for one-electron-reduced state unrestricted open-shell calculations were done. The value of the numerical integration parameter used to determine the precision of numerical integrals was 5.5. The program MOLEKEL4.3.¹⁷ was used for visualization of the orbitals.

The ground-state calculations were operated with the symmetry being restricted to T_d point group for $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$, C_1 for $[\alpha\text{-1,5-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$, C_2 for $[\alpha\text{-1,4-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$, C_{2v} for $[\alpha\text{-1,11-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$, and C_s for both $[\alpha\text{-1,2-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ and $[\alpha\text{-1,6-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$, respectively (Figure 1).

All of the calculations reported here were carried out by considering only the ions without either counterions or solvent molecules. This approximation is reasonable for the purpose of the present study since this environment was not necessary to modify either the ordering or the relative orbital energies of the cluster.^{3a}

Results and Discussion

Molecular Structures. The optimized selected bond distances of $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$ (system 1) and $[\alpha\text{-1,11-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ (system 2) are shown in Table 1. Experimental data for system 1 are abbreviated as exp^a , and the average measurement of $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ isomers is abbreviated as exp^b . These experimental data were obtained from previous reports in refs 4a and 10b. The bond lengths calculated by ZORA BP86 are shortened, which shows good consistency with experimental results, so the results reported in the following sections are based on the ZORA geometry optimizations.

The oxygen atoms in the Keggin polyanions and their derivatives can be divided into three categories: center tetrahedral oxygen (O_a), bridge oxygen (O_b and O_c), and

- (5) (a) Barcza, L.; Pope, M. T. *J. Phys. Chem.* **1973**, *77*, 1795. (b) Finke, R. G.; Droege, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7274. (c) Suslick, K. S.; Cook, J. C.; Rapko, B.; Droege, M. W.; Finke, R. G. *Inorg. Chem.* **1986**, *25*, 241. (d) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947. (e) Nomiya, K.; Kaneko, M.; Kasuga, N. C.; Finke, R. G.; Pohl, M. *Inorg. Chem.* **1994**, *33*, 1469. (f) Weiner, H.; Aiken, J. D., III; Finke, R. G. *Inorg. Chem.* **1996**, *35*, 7905. (g) Harmalker, S. P.; Leparulo, M. A.; Pope, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 4286. (h) Domaille, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 7679. (i) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947. (j) Domaille, P. J.; Watunya, G. *Inorg. Chem.* **1986**, *25*, 1239. (k) Domaille, P. J.; Harlow, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 2108. (l) Finke, R. G.; Droege, M. W.; Cook, J. C.; Suslick, K. S. *J. Am. Chem. Soc.* **1984**, *106*, 5750. (m) Canny, J.; Thouvenot, R.; Teze, A.; Herve, G.; Leparulo-Loftus, M.; Pope, M. T. *Inorg. Chem.* **1991**, *30*, 976. (n) Rapko, B. M.; Pohl, M.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 3625.
- (6) (a) Yamase, T.; Sugeta, M. *Inorg. Chim. Acta* **1990**, *172*, 131. (b) Yamase, T.; Ishikawa, E.; Asai, Y.; Kanai, S. *J. Mol. Catal. A: Chem.* **1996**, *114*, 237. (c) Ishikawa, E.; Yamase, T. *J. Mol. Catal. A: Chem.* **1999**, *142*, 61. (d) Gao, F.; Yamase, T.; Suzuki, H. *J. Mol. Catal. A: Chem.* **2002**, *180*, 97. (e) Ikeda, S.; Nishiyama, S.; Yamamoto, A.; Yamase, T.; Nishimura, C.; De Clercq, E. *J. Med. Virol.* **1993**, *41*, 191. (f) Shigeta, S.; Mori, S.; Kodama, E.; Kodama, J.; Takahashi, K.; Yamase, T. *Antiviral Res.* **2003**, *58*, 265. (g) Dan, K.; Miyashita, K.; Seto, Y.; Fujita, H.; Yamase, T. *Pharmacol. Res.* **2002**, *46*, 357. (h) Yamase, T.; Tomita, K.; Seto, Y.; Fujita, H. *Biomed. Pharm. Appl.* **1991**, *13*, 187. (i) Take, Y.; Tokutake, Y.; Inoue, Y.; Yoshida, T.; Yamamoto, A.; Yamase, T.; Nakamura, S. *Antiviral Res.* **1991**, *113*, 15. (j) Fukuma, M.; Seto, Y.; Yamase, T. *Antiviral Res.* **1991**, *327*, 16.
- (7) Knoth, W. H.; Domaille, P. J.; Roe, D. C. *Inorg. Chem.* **1983**, *22*, 198.
- (8) Domaille, P. J.; Knoth, W. H. *Inorg. Chem.* **1983**, *22*, 818.
- (9) Ozeki, T.; Yamase, T. *Acta Crystallogr., Sect. C* **1991**, *47*, 693.
- (10) (a) Nomiya, K.; Takahashi, M.; Widegren, J. A.; Aizawa, T.; Sakai, Y.; Kasuga, N. C. *J. Chem. Soc., Dalton Trans.* **2002**, 3679. (b) He, J. H.; Wang, X. H.; Chen, Y. G.; Liu, J. F.; Hu, N. H.; Jia, H. Q. *Inorg. Chem. Commun.* **2002**, *5*, 796.
- (11) (a) te Velde, G.; Bickelhaupt, F. M.; van Gisbergen, S. J. A.; Fonseca Guerra, C.; Baerends, E. J.; Snijders, J. G.; Ziegler, T. *Chemistry with ADF. J. Comput. Chem.* **2001**, *22*, 931. (b) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391. (c) ADF2002.03, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com>
- (12) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

- (13) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- (14) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
- (15) (a) Snijders, J. G.; Baerends, E. J.; Ros, P. *Mol. Phys.* **1979**, *38*, 1909. (b) Boerrigter, P. M.; Baerends, E. J.; Snijders, J. G. *Chem. Phys.* **1988**, *122*, 357. (c) Ziegler, T.; Tschinke, V.; Baerends, E. J.; Snijders, J. G.; Ravenek, W. *J. Phys. Chem.* **1989**, *93*, 3050.
- (16) (a) Chang, C.; Pelissier, M.; Durand, M. *Phys. Scr.* **1986**, *34*, 394. (b) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597. (c) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1994**, *101*, 9783. (d) van Lenthe, E.; van Leeuwen, R.; Baerends, E. J.; Snijders, J. G. *Int. J. Quantum Chem.* **1996**, *57*, 281. (e) van Lenthe, E.; Ehlers, A. E.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 8943. (f) van Lenthe, E.; Snijders, J. G.; Baerends, E. J. *J. Chem. Phys.* **1996**, *105*, 6505.
- (17) (a) Flükiger, P.; Lüthi, H. P.; Portmann, S.; Weber, J. *MOLEKEL 4.3; Swiss Center for Scientific Computing; Manno, Switzerland, 2000–2002*. (b) Portmann, S.; Lüthi, H. P. *MOLEKEL: An Interactive Molecular Graphics Tool. CHIMIA* **2000**, *54*, 766.

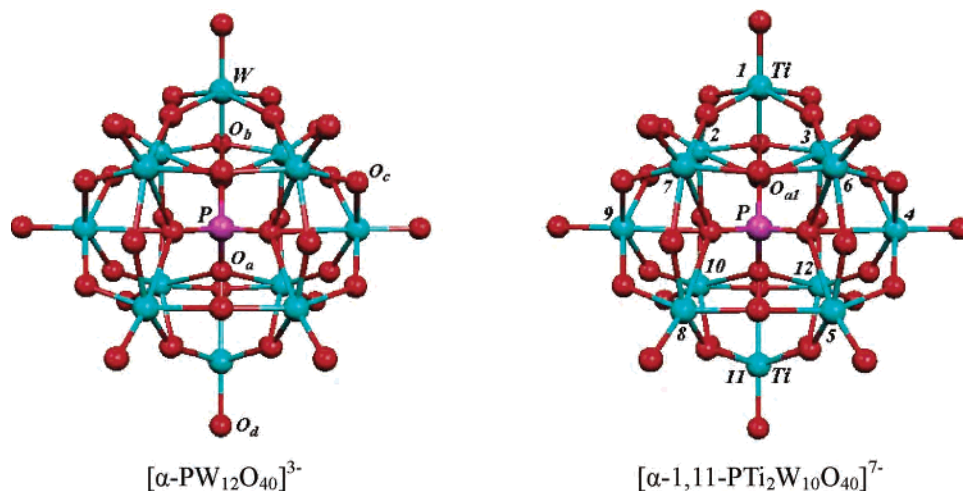


Figure 1. Calculation models.

Table 1. Selected Bond Lengths of Systems Optimized with the Same Density Functionals (in Å)

	[α -PW ₁₂ O ₄₀] ³⁻ (1)		
	TZP	TZP ^c	exp ^a
P–O _a	1.577	1.554	1.53
W–O _a	2.518	2.472	2.43
W–O _b	1.964	1.932	1.90–1.91
W–O _c	1.973	1.939	1.90–1.91
W–O _d	1.754	1.725	1.69
	[α -1,11-PTi ₂ W ₁₀ O ₄₀] ⁷⁻ (2)		
	TZP	TZP ^c	exp ^b
P–O _a	1.575–1.587	1.552–1.564	1.51–1.54
W–O _a	2.484–2.579	2.441–2.540	2.40–2.47
W–O _d	1.795–1.797	1.764–1.767	1.69–1.76
W–O _b (W ₂)	1.880–2.008	1.924–1.974	1.86–2.01
W–O _b (TiW)	1.880	1.845	1.83–1.91
W–O _c (W ₂)	1.976–2.011	1.924–1.975	1.85–1.99
W–O _c (TiW)	1.892	1.845–1.858	1.84–1.90
Ti–O _b (TiW)	2.033	2.030	1.91–1.98
Ti–O _c (TiW)	2.042	2.036	1.94–2.02

^a Reference 4a. ^b Reference 10b. ^c Adding ZORA Relativistic Method.

terminal oxygen (O_d). The bridge oxygen can be divided into corner-sharing oxygen of M₃O₁₀ corner-sharing triads, O_b, and corner-sharing oxygen of M₃O₁₀ edge-sharing triads, O_c.

Present calculations in geometry of system 1 exhibit a high agreement with experimental measurements, only with quite a little exception in larger metal-terminal and metal-tetrahedral oxygen bond lengths. The deviations of average 0.04 Å are consistent with a recent review of Poblet.^{3d} It is impossible to compare the calculated results with the measurements one by one for hard separation experimentally in systems 2–6.

The selected bond distances of optimized systems, [α -1,5-PTi₂W₁₀O₄₀]⁷⁻ (system 3), [α -1,4-PTi₂W₁₀O₄₀]⁷⁻ (system 4), [α -1,2-PTi₂W₁₀O₄₀]⁷⁻ (system 5), and [α -1,6-PTi₂W₁₀O₄₀]⁷⁻ (system 6), with the same density functionals are presented in Table 2. It indicates that the bond lengths of Ti–O are longer than those of W–O, because the ionic radius of Ti^{IV} (0.68 Å) is bigger than that of W^{VI} (0.62 Å). In order to explain the influence of Ti-substitution on the bond lengths of P–O_a, the bond lengths of P–O_{a1} in Ti-substituted systems are studied considering only one titanium atom based on quite

Table 2. Selected Bond Lengths of Systems Optimized with ZORA Relativistic Method (in Å)

	[α -1,5-PTi ₂ W ₁₀ O ₄₀] ⁷⁻ (3)		[α -1,4-PTi ₂ W ₁₀ O ₄₀] ⁷⁻ (4)	
P–O _a	1.546–1.572	1.548–1.569		
W–O _a	2.411–2.535	2.443–2.502		
W–O _d	1.764–1.767	1.765–1.768		
W–O _b (W ₂)	1.889–2.033	1.870–2.062		
W–O _b (TiW)	1.830–1.881	1.829–1.847		
W–O _c (W ₂)	1.902–2.038	1.881–2.081		
W–O _c (TiW)	1.847–1.900	1.842–1.859		
Ti–O _b (TiW)	1.979–2.071	2.011–2.059		
Ti–O _c (TiW)	1.971–2.064	2.016–2.048		
	[α -1,2-PTi ₂ W ₁₀ O ₄₀] ⁷⁻ (5)		[α -1,6-PTi ₂ W ₁₀ O ₄₀] ⁷⁻ (6)	
P–O _a	1.530–1.574	1.549–1.575		
W–O _a	2.407–2.556	2.437–2.554		
W–O _d	1.764–1.770	1.763–1.769		
W–O _b (W ₂)	1.861–2.084	1.879–2.054		
W–O _b (TiW)	1.803–1.814	1.825		
W–O _c (W ₂)	1.888–2.062	1.876–2.087		
W–O _c (TiW)	1.835	1.814–1.827		
Ti–O _b (TiW)	2.102–2.183	2.065		
Ti–O _c (TiW)	2.063	2.097–2.176		

complicated computation, because the substituted site of the other titanium atom (Ti₁ in Figure 1) is same in all isomers. Results show that the longer Ti–O_{a1} distances are, and the longer the bond lengths of P–O_{a1} are. In Ti-substituted systems the bond lengths of P–O_{a1} are shorter than those of phosphotungstate (system 1).

Mulliken Charge Analysis in Keggin Anions. The Mulliken charges are not too significant sometimes, but in general, the charge differences are much more believable.^{4a} The net charges being computed for systems 1–6 are listed in Table 3, and charge analysis of Mulliken is performed and discussed as follows.

(1) In Ti-substituted systems and phosphotungstate, the negative charges of bridge oxygen are larger than those of terminal oxygen, especially O_c(TiTi) and O_b(TiTi) in systems 5 and 6, which have the same values, –0.94 e. This indicates that the basicity of bridge oxygen linked to two titaniums is higher and tends to accept protons.

(2) The transferred charges from O_d to tungstens and titaniums are bigger than those from O_b and O_c in both Ti-substituted systems and phosphotungstate, so the bond of M=O_d is stronger.

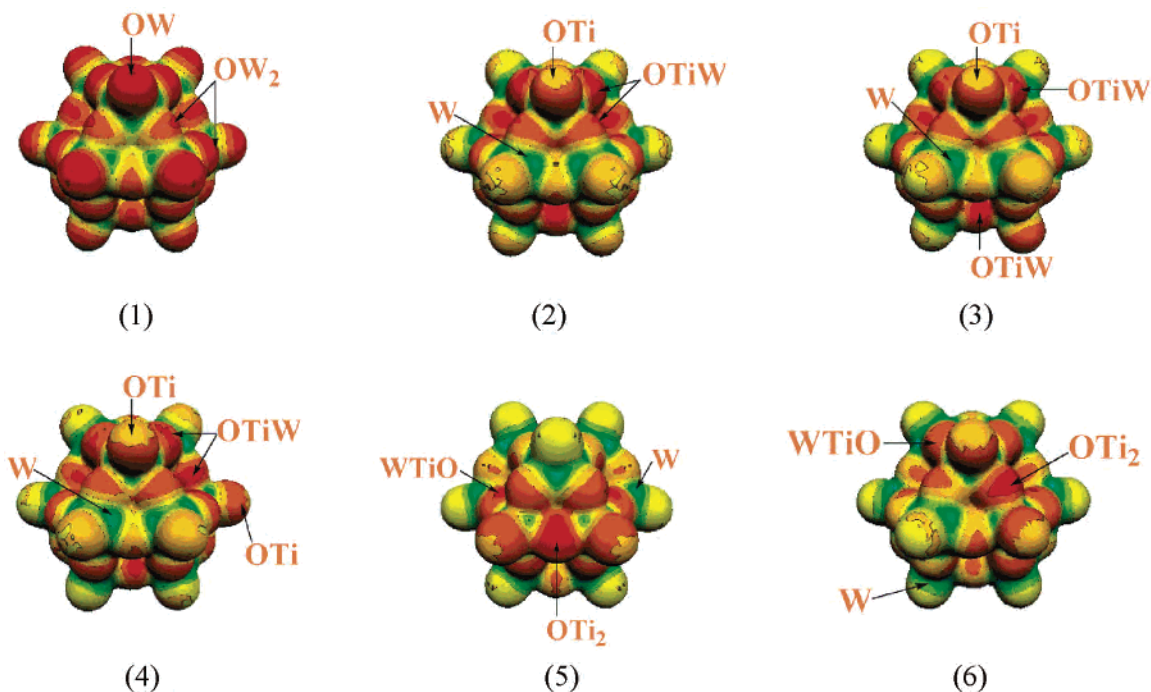


Figure 2. Molecular electrostatic potentials of $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$ and $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ isomers (red regions represent nucleophilic areas whereas green regions represent electrophilic areas).

Table 3. Net Charges Computed for $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$ and $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ Isomers

	$[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$ (1)	$[\alpha\text{-1,11-PTi}_2\text{-W}_{10}\text{O}_{40}]^{7-}$ (2)	$[\alpha\text{-1,5-PTi}_2\text{-W}_{10}\text{O}_{40}]^{7-}$ (3)
PO ₄	-1.66	-1.63	-1.64
O _d (W)	-0.69	-0.83	-0.83
O _d (Ti)		-0.84(9)	-0.85(1)
O _b (W ₂)	-0.90	-0.91	-0.90
O _c (W ₂)	-0.90	-0.92	-0.92
O _b (TiW)		-0.88	-0.88
O _c (TiW)		-0.89	-0.90
Ti		1.68	1.68
W	2.37	2.29	2.29
	$[\alpha\text{-1,4-PTi}_2\text{-W}_{10}\text{O}_{40}]^{7-}$ (4)	$[\alpha\text{-1,2-PTi}_2\text{-W}_{10}\text{O}_{40}]^{7-}$ (5)	$[\alpha\text{-1,6-PTi}_2\text{-W}_{10}\text{O}_{40}]^{7-}$ (6)
PO ₄	-1.64	-1.62	-1.64
O _d (W)	-0.83	-0.83	-0.83
O _d (Ti)	-0.84(4)	-0.86(1)	-0.86(3)
O _b (W ₂)	-0.90	-0.91	-0.90
O _c (W ₂)	-0.91	-0.92	-0.92
O _b (TiW)	-0.88	-0.84	-0.88
O _c (TiW)	-0.89	-0.88	-0.85
O(TiTi)		-0.94	-0.94
Ti	1.67	1.63	1.65
W	2.29	2.29	2.29

(3) By comparison with the charges of O_d in Ti-substituted systems and those in the phosphotungstate system, it can be found that the transferred charges from terminal oxygens to tungstens and titaniums decrease after Ti-substitution, especially in O_d(Ti), which shows that the Ti=O_d bond is weaker than the W=O_d bond in Ti-substitution. Moreover, by comparing with the charges of O_d(Ti) in different Ti-substituted systems, it can be concluded that the order of transferred charges from O_d(Ti) to titaniums is system 4 > system 2 > system 3 > system 5 > system 6, and this is also the order of bond intensity of Ti=O_d. It may suggest

that system 6 can easily form covalent bonding with organometallic fragments on the titanium surface.

(4) For system 1, the Mulliken analysis assigns an electronic charge of $-1.66 e$ to PO₄. The negative charges on the PO₄ tetrahedron in $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ isomers decrease, but the decreasing value is quite small. So, here it is proposed that Ti-substitution does not change the net charge on the internal tetrahedron because the additional charges which come from Ti atoms substituted W atoms may go to the outer sphere of clusters.

Localization of the Activating Proton in $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ Isomers. The protonation of $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ could lead to creating many isomers depending on the protonation and anchoring sites of the proton. However, a qualitative analysis of the relative nucleophilicity of the external regions of the POM is feasible by the electrostatic potential (EP) function.⁴ Molecular electrostatic potentials for $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$ and $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ isomers are shown in Figure 2. The red areas represent regions of negative electrostatic potentials (nucleophilic sites), and the green areas identify regions of positive or less negative electrostatic potentials. The different color values of each system in Figure 2 should be noticed. In fact, the basicity of $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ isomers is much higher than that of system 1 owing to the charge difference. A simple analysis of MEP representations below suggests that the preferred protonation site corresponds to bridge oxygens (O_b and O_c) and terminal oxygens (O_d) in system 1, to bridge oxygens (OTi₂ and OTiW) and less terminal oxygens (OTi) in systems 2–6, and especially to bridge oxygens bonded to titaniums (OTi₂) in systems 5 and 6, respectively. However, the terminal oxygens bonded to W (OW) are the least nucleophilic sites in Ti-substituted systems.

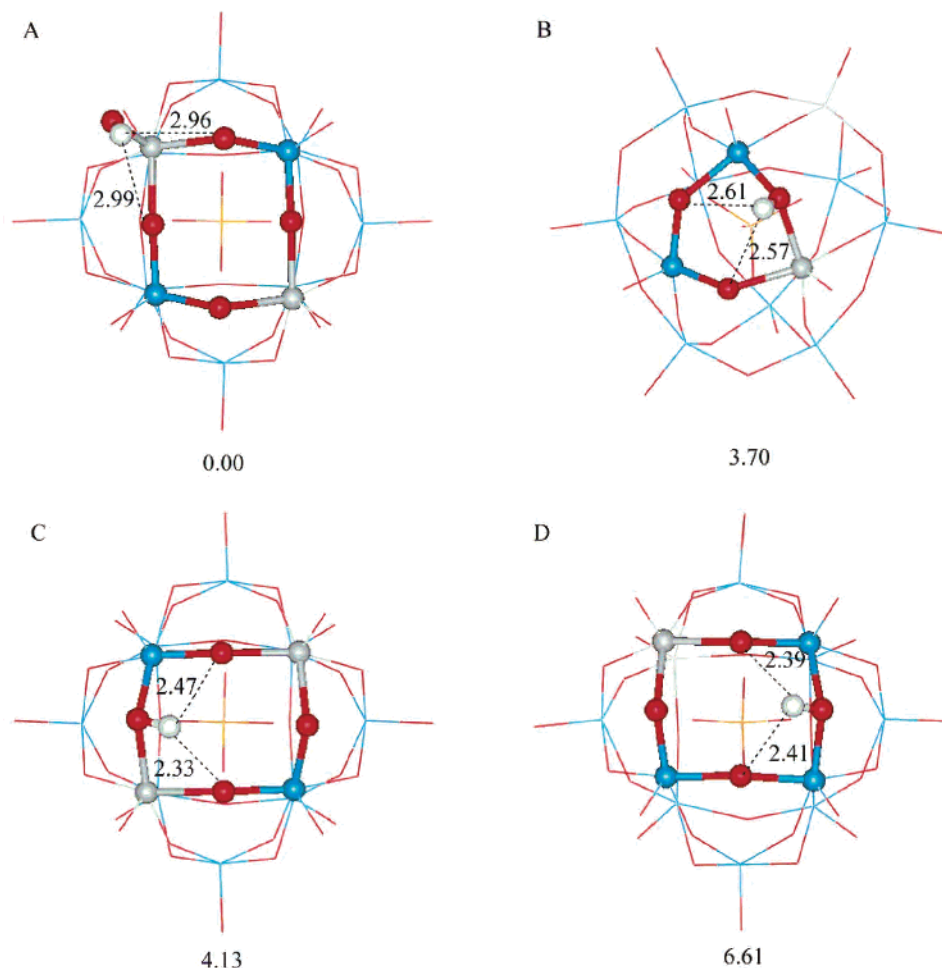


Figure 3. Optimized structures, relative energies (in kcal·mol⁻¹) in gas phase, and H···O distances (in Å) for several isomers of [α-1,4-HPTi₂W₁₀O₄₀]⁶⁻.

According to the qualitative analysis mentioned above, a quantitative description is obtained by the study of the protonated species, [α-1,4-HPTi₂W₁₀O₄₀]⁶⁻. Three kinds of protonated oxygens, bridge oxygen (OTiW) belonged to the Ti₂W₂O₄ ring, terminal oxygen (OTi), and bridge oxygen (OW₂), are selected to analyze the most basic site in system 4 (Figure 3). When these oxygens are protonated, several local minima are found. In agreement with the experimental characterization⁸ for protonation site in [H₂PTi₂W₁₀O₄₀]⁵⁻, the DFT calculations show that structure A (Figure 3A) is the most stable, where the proton is roughly equidistant from two bridging oxygens. Domaille and Knoth⁸ have concluded that the terminal oxygen on titanium is the most likely protonation site by ¹⁷O NMR studies; i.e., H₂PTi₂W₁₀O₄₀⁵⁻ should be best formulated as (HOTi)₂W₁₀PO₃₈⁵⁻. In structure B, the hydrogen is anchored toward the center of the nearest TiW₂O₃ ring. This form is 3.70 kcal·mol⁻¹ higher than the most stable structure A in the gas phase. While in structure C the hydrogen is oriented toward the center of the nearest Ti₂W₂O₄ ring, the relative energy of structure A is 4.13 kcal·mol⁻¹. Structure D is quite unstable, because the bridge oxygen (OW₂) site shows less basicity.

However, all of these calculations reported here were carried out considering only the gas phase without solution. Poblet and co-workers^{4e} recently reported that a large

stabilization was observed for those anions with the proton exposed to the solution when the effect of the solvent was included in the calculations. Then we assume that the energy of systems will be stabilized by interaction of the proton with the solvent, especially for structure A. Therefore, TiO–H protonated anions could still be the most stable structure in solution. In addition, Poblet and co-workers have concluded that both the intrinsic basicity of an oxygen site and H···O interactions are of great importance in determining the protonation site in a POM, but Figure 3 illustrates clearly that H···O interactions show the opposite effect on the stability of the polyanions, so we presume that the factors of determining the protonation site should be related to the given POM clusters.

Electronic Properties of Phosphotungstate and Ditungstenium Substitution. The highest occupied molecular orbitals (HOMOs) in [α-PW₁₂O₄₀]³⁻ formally delocalize over bridge oxygens and slightly on tungstens, while the lowest unoccupied d-metal orbitals delocalize over tungstens in 67%, and p-oxygen orbitals account for about 29% (Figure 4). The lowest unoccupied molecular orbitals (LUMOs) are the metallic orbitals with an antibonding property between the metal and oxygen orbitals. However, comparing with [α-PW₁₂O₄₀]³⁻, the frontier molecular orbitals of Ti-substituted systems significantly change. As presented in

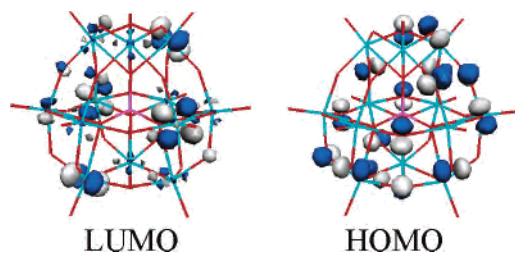


Figure 4. LUMO and HOMO for $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$.

Figure 5, the orbital diagram of the frontier molecular orbitals of $[\alpha\text{-1,6-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ (system 6) is illustrated, and we could draw the following conclusion.

(1) For occupied orbitals, the bands of occupied orbitals of Ti-substituted isomers formally delocalize over the p-oxygen orbitals, and slightly over the p- and d-titanium orbitals, and those oxygens are closer to the titaniums. In systems 5 and 6, the HOMOs thoroughly delocalize over the bridge oxygen linked to two titaniums, $\text{O}(\text{TiTi})$, and the terminal oxygen linked to titaniums, $\text{O}_d(\text{Ti})$. The $\text{Ti}(\text{p})=\text{O}_d(\text{p})$ bond has an antibonding character. The HOMO in system 2 mostly delocalizes over both sides of two symmetric titaniums.

(2) For unoccupied orbitals, the LUMOs of Ti-substituted isomers delocalize mostly over the d-tungsten orbitals away from titaniums (ca. 60%), partially over the p-oxygen orbitals, and slightly over the d-titanium orbitals. These results show that the d-tungsten orbitals play an important role in redox reaction of Ti-substituted systems, which is similar to system 1. However, the delocalization of d-tungsten orbitals in system 1 is different from that in five Ti-substituted systems, which means that Ti-substitution changes the site of redox reaction. Besides, the unoccupied bands $\text{Ti}(\text{d})-\text{O}_b(\text{p})$ and $\text{Ti}(\text{d})-\text{O}_c(\text{p})$ have a bonding interaction in systems 5 and 6, but there is mostly antibonding participation of $\text{M}(\text{d})-\text{O}_b(\text{p})$, $\text{M}(\text{d})-\text{O}_c(\text{p})$, and $\text{W}(\text{d})=\text{O}_d(\text{p})$ in the other of isomers.

Stability of $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ Isomers. So far, five isomers of $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ have not been purified completely, and the experimental products usually contain a mixture, in which one isomer, $[\alpha\text{-1,4-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ with C_2 symmetry, predominates.⁸ Here, their total bonding energies are analyzed. According to the transition state method of Ziegler and Rauk,¹⁸ the molecular bonding energy (E_B) can be decomposed as

$$E_B = E_E + E_P + E_O$$

where E_E , E_P , and E_O are electrostatic interaction, Pauli repulsion, and orbital mixing terms, respectively. The descriptions of the physical meaning of these properties have been given by Landrum, Goldberg, Hoffmann,¹⁹ and Baerends.²⁰ E_E is electrostatic term whose contribution is primarily

Table 4. Orbital (E_O), Pauli (E_P), and Electrostatic (E_E) Contributions (in eV) to the Bonding Energies (E_B 's) of Five $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ Isomers

	2	3	4	5	6
E_O	-1112.6743	-1112.5108	-1112.1764	-1110.3178	-1111.3419
E_E	-386.5434	-386.4687	-386.2624	-385.4198	-385.6831
E_P	1080.6608	1080.4025	1079.7465	1077.5077	1078.8075
E_B	-418.5571	-418.5769	-418.6923	-418.2300	-418.2177

dominated by the nucleus–electron attractions. The Pauli repulsion²¹ acts as the destabilization which is caused by the larger energy shift of antibonding orbitals to bonding orbitals. E_O arises due to the mixing of occupied and unoccupied orbitals. So, E_E and E_O are stabilizing effect.

The bonding energy, as well as orbital-mixing, Pauli repulsion, and electrostatic-interaction contributions to the bonding energies of systems 2–6 are given in Table 4. The calculated total bonding energies (E_B 's) of the whole systems show that the stability is the following: system 4 > system 3 > system 2 > system 5 > system 6. The bonding energy of system 4 is the lowest among all systems, and as a result, it is the most stable one, which is consistent with experimental results. However, the bonding energy of system 6 is the highest, leading the polyanion of system 6 to be more active. This is also one of the reasons for formation of a dimer in system 6. Considering the effect of each physical term, E_O and E_P serve chiefly as contributions to the stability of the polyanions and E_E is minor. These results correspond with the Ti-substituted sites. In systems 5 and 6, di-Ti-substituted sites are adjacent to each other, and Ti–O bond lengths are relatively longer (seen in Tables 1 and 2). The longer distances should be associated with the smaller overlap of orbital and charge distribution, so E_O and E_E have smaller values and systems 5 and 6 are less stable, and then they are more active, especially for system 6. E_P plays an important role in the stability of systems 2, 3, and 4. But among them, for system 4 the influence of E_P is relatively minor; i.e., the destabilization is smaller, so it is more stable than systems 2 and 3. Systems 2 and 3 should have a similar stability due to their quite close E_P values.

Redox Properties of Ditungsten Substitution. Changes of the electronic properties are related to the occupied orbitals, and they also affect the lowest unoccupied orbitals, thus leading to the change in the redox properties of these clusters. Figure 6 presents a molecular orbital diagram for $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$ and $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ isomers. It is well-known that if tungsten is substituted by a higher electronegative atom in $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$, such as Mo, V, etc., the redox properties of a substituted system can be changed remarkably. In present calculations, the electronegativity of Ti and W is equivalent, so this structural difference arising from different Ti-substituted sites determines the electronic and redox properties. As shown in Figure 6, the HOMO–LUMO gaps (ΔE 's) change for different symmetries of systems. For systems 5 and 6, ΔE decreases by 0.369 and 0.392 eV, respectively. However, in systems 2, 3, and 4 ΔE increases

(18) (a) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558. (b) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1755. (c) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.

(19) Landrum, G. A.; Goldberg, N.; Hoffmann, R. *J. Chem. Soc., Dalton Trans.* **1997**, 3605.

(20) Bickelhaupt, F. M.; Baerends, E. J. *Rev. Comput. Chem.* **2000**, *15*, 1.

(21) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

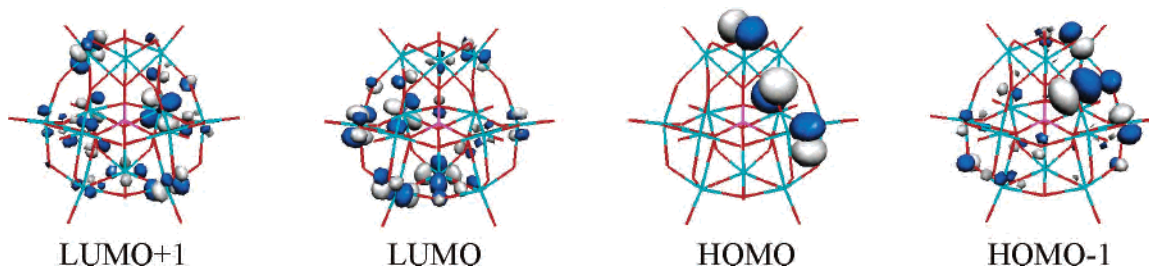


Figure 5. Schematic orbital diagram of the frontier molecular orbitals of $[\alpha\text{-}1,6\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$.

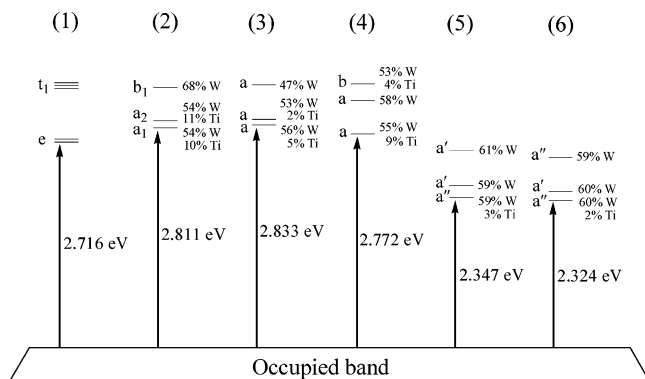


Figure 6. Molecular orbital diagram for $[\alpha\text{-PW}_{12}\text{O}_{40}]^{3-}$ and $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ isomers.

Table 5. Spin Polarizations ($\alpha\text{-}\beta$ Electrons) for Five One-Electron-Reduced $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$ Isomers

anion	spin polarization	
	W	Ti
$[\alpha\text{-}1,11\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$	0.79	0.24
$[\alpha\text{-}1,5\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$	0.84	0.18
$[\alpha\text{-}1,4\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$	0.81	0.22
$[\alpha\text{-}1,2\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$	0.91	0.03
$[\alpha\text{-}1,6\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$	0.90	0.03

slightly by 0.095, 0.117, and 0.056 eV, respectively. From these results and consideration of the higher negative charge in the Ti-substituted derivatives, it can be concluded that in systems 2, 3, and 4 the stability is higher, but redox ability is weaker because of the higher energies of the LUMO in Ti-substituted isomers, while for systems 5 and 6 the stability is weaker, but redox ability is higher. Moreover, the LUMO, LUMO + 1, and LUMO + 2 localize mainly on the tungsten centers, which shows that the W orbitals easily obtain the additional electron.

Spin polarizations given in Table 5 confirm our qualitative predictions based on the molecular orbitals of the oxidized species, and besides, extra polarization in the molecule yields a population of 0.24 spin α electrons on W_4 (Figure 1) for $[\alpha\text{-}1,11\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$, 0.20 on W_{12} for $[\alpha\text{-}1,5\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$, 0.25 on W_9 for $[\alpha\text{-}1,4\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$, 0.19 on W_4 for $[\alpha\text{-}1,2\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$, and 0.21 on W_8 for $[\alpha\text{-}1,6\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$, which suggest that W atoms have a greater ability to capture an additional electron than Ti atoms. Hence, the additional electrons in the one-electron-reduced species $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$ isomers are delocalized among the tungsten centers.

From Table 6, one-electron-reduced calculation results of the five $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$ isomers indicate that five reduced isomers have almost the same stability as the oxidized partners.

Table 6. Bonding Energies (E_B 's) of Five One-Electron-Reduced $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$ Isomers (in eV)

anion	E_B
$[\alpha\text{-}1,11\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$	-402.6204
$[\alpha\text{-}1,5\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$	-402.6146
$[\alpha\text{-}1,4\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$	-402.8016
$[\alpha\text{-}1,2\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$	-402.3690
$[\alpha\text{-}1,6\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$	-402.3577

Conclusions

DFT calculations have been first carried out on five $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ isomers to investigate electronic properties, redox properties, protonation, and stability.

(1) A simple analysis of these MEP representations suggests that the preferred protonation site corresponds to bridge oxygens (O_b and O_c) and terminal oxygens (O_d) in system 1, bridge oxygens and less terminal oxygens bonded to Ti (OTi) in systems 2–6, especially bridge oxygens bonded to titaniums (OTi₂) in system 5 and 6, respectively. The DFT calculations carried out on the protonated anion $[\alpha\text{-}1,4\text{-HPTi}_2\text{W}_{10}\text{O}_{40}]^{6-}$ suggest that the most stable structure is formed preferentially after protonation of the Ti–O site in the gas phase, which is consistent with the experimental results. Also, it can presume that TiO–H protonated anions could still be the most stable structure in solution.

(2) The bands of occupied orbitals of Ti-substituted isomers formally delocalize over the p-oxygen orbitals, and slightly over the p- and d-titanium orbitals, and those oxygens are closer to the titaniums. The LUMOs of Ti-substituted isomers delocalize mostly over the d-tungsten orbitals away from titaniums (ca. 60%), partially over the p-oxygen orbitals, and slightly over the d-titanium orbitals. Also, the ability of electronic transfer is enhanced by Ti-substitution.

(3) The total bonding energies (E_B 's) of $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ isomers lead into the following order of stability: system 4 > system 3 > system 2 > system 5 > system 6. Five reduced isomers have a similar stability to the oxidized partners. The additional electrons in the one-electron-reduced species, $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{8-}$ isomers, are delocalized mainly around the tungsten centers.

(4) The structural difference of $[\alpha\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ isomers determines the electronic and redox properties. The d-tungsten orbitals play an important role in redox activity. Among the five isomers, the stability of $[\alpha\text{-}1,2\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ and $[\alpha\text{-}1,6\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ is weaker and redox ability is higher, while for $[\alpha\text{-}1,5\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$, $[\alpha\text{-}1,4\text{-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$,

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and $[\alpha\text{-1,11-PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$ the stability is higher, but redox ability is weaker.

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