Inorg. Chem. **2003**, *42*, 2634–2638

Inorganic Chemistry
Article

Relative Stability in α- and β-Wells–Dawson Heteropolyanions: A DFT Study of $[P_2M_{18}O_{62}]^{n-}$ (M = W and Mo) and $[P_2W_{15}V_3O_{62}]^{n-}$

Xavier López, Carles Bo, and Josep-M. Poblet*

Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Imperial Tarraco 1,
43005 Tarragona, Spain

José Pedro Sarasa

Departamento de Química Física y Química Orgánica, Universidad de Zaragoza,
Ciudad Universitaria s/n, 50009 Zaragoza, Spain

Received December 3, 2002

To determine the relative stability of α and β rotational isomers of the Wells–Dawson structure, the energies of some fully oxidized, single- and 2-fold-reduced systems were calculated by means of DFT calculations. The thermodynamics of the α/β equilibrium for P_2M_{18} Wells–Dawson anions is slightly shifted toward the α structure, but the difference in stability is smaller than in the Keggin anions. Tungstates (2:18) and vanadotungstates (2:3:15) show minimal redox differences between isomers, as the electronic structure of the frontier orbitals appears to be nearly the same. In addition, an alternative arrangement is proposed that have long and short Mo–O bonds in β-P_2Mo_{18} with an idealized C_3 symmetry. This arrangement was computed to be about 8.2 kcal mol^{-1} more stable than the nonalternate framework of C_{3v} symmetry. The P_2Mo_{18} is the Wells–Dawson anion for which the α/β equilibrium most resembles that of the Keggin anions.

Introduction

In a previous study we used DFT calculations to make a detailed analysis of the factors that govern the relative stability of the α and β isomers of the Keggin anion, $[XM_{12}O_{40}]^{n-}$ (M = W, Mo, and X, a main group element).[1] The α isomer has T_d symmetry[2] and the β isomer, of C_{3v} symmetry, is derived from a 60° rotation of one M_3O_{13} triad about a 3-fold axis of the α form.[3] DFT calculations also showed that the metallic (*blue*) electrons incorporated in the $M_{12}O_{36}$ framework and the greater stability of the β isomer are closely related.[1] It is well-known that β structures are reduced at more positive potentials than α isomers.[4] This gain in stability may be because there is a reduction in symmetry when going from α to β and a subsequent decrease in the energy of the LUMO. Using the clathrate model, which suggests that a Keggin anion can be viewed as a charged $[XO_4]^{n-}$ anion encapsulated by a neutral $M_{12}O_{36}$ cage,[5] we showed that several factors compete in the thermodynamics of Keggin anions: the greater intrinsic stability of the most symmetric α organization of the oxo ligands (O^{2-}) and d^0 metal ions and the greater polarizability of the less symmetric neutral β-$M_{12}O_{36}$ cage. The latter is probably responsible for the greater stability of the β isomer in highly charged anions. Both theoretical[1] and the experimental[6] studies coincide in the ordering of the α/β relative stability of Keggin anions with X.

The rotational isomerism of Keggin structures also takes place in Wells−Dawson[7] (WD) heteropolyanions, with general formula $[X_2M_{18}O_{62}]^{n-}$ (Figure 1). WD structures formally consist of two XM_9 halves linked by almost linear M−O−M bonds (∼162°). Pope, in the mid-60s,[8] and Contant's group[9] explored the electrochemistry of X_2M_{18} and mixed addenda derivatives. They found that β anions also

---

* Corresponding author. E-mail: poblet@quimica.urv.es.

(1) López, X.; Maestre, J. M.; Bo, C.; Poblet, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 9571−9576.
(2) Keggin, J. F. *Nature* **1933**, *131*, 908.
(3) Baker, L. C. W.; Figgis, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 3794−3797.
(4) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983.
(5) Day, V. W.; Klemperer, W. G. *Science*. **1985**, *228*, 533−541.
(6) Weinstock, I. A.: Cowan, J. J.; Barbuzzi, E. M. G.; Zeng, H.; Hill, C. L. *J. Am. Chem. Soc.* **1999**, *121*, 4608−4617. Newiwert, W. A.; Cowan, J. J.; Hardcastle, K. I.; Hill, C. L.; Weinstock, I. A. *Inorg. Chem.* **2002**, *41*, 6950.
(7) Dawson, B. *Acta Crystallogr.* **1953**, *6*, 113. D'Amour, H. *Acta Crystallogr., Sect C.* **1976**, *32*, 729.

10.1021/ic0262280 CCC: $25.00

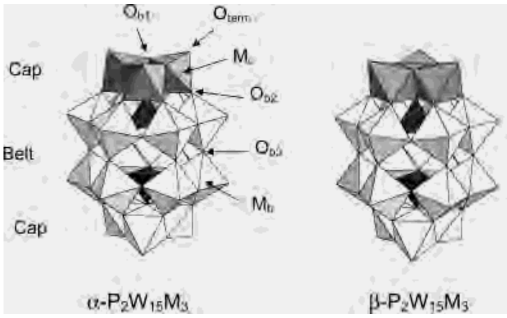

Figure 1. Polyhedral representation of the α and *β* isomers of the Wells−Dawson structure. The shaded octahedrons are those involved in the rotational isomerism and the metal substitution. The nonsubstituted α and *β* forms have D_{3h} and C_{3v} symmetry, respectively. On the other hand, the symmetry of both the α- and *β*-substituted frameworks (in the shaded positions) is C_{3v}. P_2Mo_{18} clusters have special structures (see text). Important oxygen and metal positions are labeled for further discussion.

reduce at more positive potentials than the α forms, although the difference is smaller than in Keggin pairs. Here we extend our previous studies on Keggin[1] and α-WD heteropolyanions[10] to analyze the α/*β* isomerism in WD structures by means of DFT calculations. In particular, we analyze the relative stability of the α and *β* isomers for $[P_2Mo_{18}O_{62}]^{6-}$, $[P_2W_{18}O_{62}]^{6-}$, and $[P_2W_{15}V_3O_{62}]^{9-}$,[11] as well as the effect of the single and double reduction on this equilibrium. Although the use of quantum chemistry methods to model the physical and chemical properties of POMs is still incipient, several theoretical groups have made progress in this area in the last 10 years.[1,10,12]

Theoretical Details

All the calculations presented here were carried out using the density-functional methodology, implemented in the ADF2000 program.[13] We used the local density approximation (LDA) characterized by the electron gas exchange (Xα) with $\alpha = 2/3$, together with the Vosko−Wilk−Nusair[14] (VWN) parametrization for the correlation. Becke[15] and Perdew[16] nonlocal corrections were used for the exchange and correlation energy, respectively. The basis functions were Slater-type sets. Triple-ζ + polarization basis sets were used to describe the valence electrons of all the atoms. The internal or core electrons (1s and 2s shells for phosphorus, 1s to 2sp for vanadium, 1s to 3spd for molybdenum, and 1s to 4spd for tungsten) were described by means of single Slater functions. Quasirelativistic corrections were used for the core electrons alongside the Pauli formalism with corrected core potentials. The quasirelativistic frozen core shells were generated with the auxiliary program DIRAC,[13] included in the ADF2000 package. The open-shell electronic configurations were described with the unrestricted methodology. The discussion of all the anions is based on the fully optimized geometries in each oxidation state.

Results and Discussion

Geometry optimizations performed on the α and *β*[3,17] isomers of the title anions led to the structures listed in Table 1. The α isomer of P_2W_{18} was computed under the constraints of D_{3h} symmetry group, whereas for the corresponding *β* isomer the symmetry of the molecule is C_{3v}. As we will discuss below, the analogous molybdates have less symmetry. In general, the geometries of the heteropolyanions are very well reproduced at the present level of theory. The largest discrepancy appears in the $W-O_{term}$ oxygen bonds, which are systematically underestimated by an average of 0.05 Å.[7,24] Deviations in the terminal bonds should not modify the reduction properties discussed here, since they would essentially affect the energy of the d_{xz}- and d_{yz}-type orbitals, which are not the lowest. The reader will notice from Table 1 that the geometrical differences between isomers of the same formula are very small. Only the $M_b–O_{b3}–M_b$ angle

---

(8) (a) Pope, M. T.; Papaconstantinou, E. *Inorg. Chem.* **1967**, *6*, 1147. (b) Papaconstantinou, E.; Pope, M. T. *Inorg. Chem.* **1967**, *6*, 1152. (c) Varga, G. M.; Papaconstantinou, E.; Pope, M. T. *Inorg. Chem.* **1970**, *9*, 662. (d) Papaconstantinou, E.; Pope, M. T. *Inorg. Chem.* **1970**, *9*, 667.

(9) Some recent publications: (a) Keita, B.; Belhouari, A.; Nadjo, L.; Contant, R. *J. Electroanal. Chem.* **1998**, *442*, 49−57. (b) Keita, B.; Girard, F.; Nadjo, L.; Contant, R.; Canny, J.; Richet, M. *J. Electroanal. Chem.* **1999**, *478*, 76−82. (c) Keita, B.; Lu, Y. W.; Nadjo, L.; Contant, R.; Abbessi, M.; Canny, J.; Richet, M. *J. Electroanal. Chem.* **1999**, *477*, 146−157. (d) Contant, R.; Abbessi, M.; Canny, J.; Richet, M.; Keita, B.; Belhouari, A.; Nadjo, L. *Eur. J. Inorg. Chem.* **2000**, 567−574. (e) Keita, B.; Lu, Y. W.; Nadjo, L.; Contant, R. *Eur. J. Inorg. Chem.* **2000**, 2463−2471.

(10) López, X.; Bo, C.; Poblet, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 12574.

(11) We will use the shorthand notation, skipping oxygens and total charge from the molecular formula. For example, $[P_2W_{18}O_{62}]^{6-}$ is represented by P_2W_{18}.

(12) Kempf, J. Y.; Rohmer, M.-M.; Poblet, J.-M.; Bo, C.; Bénard, M. *J. Am. Chem. Soc.* **1992**, *114*, 1136. Rohmer, M.-M.; Benard, M. *J. Am. Chem. Soc.* **1994**, *116*, 6959. Rohmer, M.-M.; Devemy, J.; Wiest, R.; Benard, M. *J. Am. Chem. Soc.* **1996**, *118*, 13007. Maestre, J. M.; Sarasa, J. P.; Bo, C.; Poblet, J.-M. *Inorg. Chem.* **1998**, *37*, 3071. Bardin, B. B.; Bordawekar, S. V.; Neurock, M.; Davis, R. J. *J. Phys. Chem. B.* **1998**, *102*, 10817. Maestre, J. M.; Bo, C.; Poblet, J.-M.; Casañ-Pastor, N.; Gomez-Romero, P. *Inorg. Chem.* **1998**, *37*, 3444. Duclusaud, H.; Borshch, S. A. *Inorg. Chem.* **1999**, *38*, 3489. Bardin, B. B.; Davis, R. J.; Neurock, M. *J. Phys. Chem. B.* **2000**, *104*, 3556. Duclusaud, H.; Borshch, S. A. *J. Am. Chem. Soc.* **2001**, *123*, 2825. Bridgeman, A. J.; Cavigliasso, G. *Inorg. Chem.* **2002**, *41*, 3500; Bridgeman, A. J.; Cavigliasso, G. *J. Phys. Chem.* **2002**, *106*, 6114. Bridgeman, A. J.; Cavigliasso, G. *Inorg. Chem.* **2002**, *41*, 1761. Bridgeman, A. J.; Cavigliasso J. *Chem. Soc., Dalton Trans.* **2002**, 2244−2249. Bridgeman, A. J.; Cavigliasso *Polyhedron* **2002**, *21*, 2201. Bridgeman, A. J.; Cavigliasso *Chem. Phys.* **2002**, *279*, 143.

(13) *ADF 2000.01*; Department of Theoretical Chemistry, Vrije Universiteit, Amsterdam. Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41−51. Versluis, L.; Ziegler, T. *J. Chem. Phys.* **1988**, *88*, 322−328. Te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84−98. Fonseca Guerra, C.; Snijders, J. G.; Te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391−403.

(14) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(15) Becke, A. D. *J. Chem. Phys.* **1986**, 84, 4524; *Phys. Rev.* **1988**, A38, 3098.

(16) Perdew, J. P. *Phys. Rev.* **1986**, *B33*, 8882; **1986**, *B34*, 7406.

(17) Acerete, R.; Harmalker, S.; Hammer, C. F.; Pope, M. T.; Baker, L. C. W. *J. Chem. Soc., Chem. Commun.* **1979**, 777. Massart, R.; Contant, R.; Fruchart, J. M.; Ciabrini, J. P. Fournier, M. *Inorg. Chem.* **1977**, *16*, 2916.

(18) Maestre, J. M.; López, X.; Bo, C.; Casañ-Pastor, N.; Poblet, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 3749−3758. Rohmer, M. M.; Bénard, M.; Blaudeau, J. P.; Maestre, J. M.; Poblet, J. M. *Coord. Chem. Rev.* **1998**, *178−180*, 1019.

(19) Kozik, M.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1986**, *108*, 8, 2748. Kozik, M.; Baker, L. C. W. *J. Am. Chem. Soc.* **1987**, *109*, 3159. Casañ-Pastor, N.; Baker, L. C. W. *J. Am. Chem. Soc.* **1992**, *114*, 10384 and references therein.

(20) Suaud, N.; Gaita-Ariño, A.; Clemente-Juan, J. M.; Sánchez-Marín, J.; Coronado, E. *J. Am. Chem. Soc.* **2002**, *124*, 15134. Borrás-Almenar, J. J.; Clemente-Juan, J. M.; Coronado, E.; Tsukerblat, B. S. *Chem. Phys.* **1995**, *195*, 1. Borshch, S. A.; Bigot, B. *Chem. Phys. Lett.* **1993**, *212*, 398.

(21) Anderson, T. M.; Hill, C. L. *Inorg. Chem.* **2002**, *41*, 4252.

(22) Kazanskii, L. P.; Fedotov, M. A. *J. Chem. Soc., Chem. Commun.* **1980**, 644.

(23) Pope, M. T. *Inorg. Chem.* **1976**, *15*, 2008. Garvey, J. F.; Pope, M. T. *Inorg. Chem.* **1978**, *17*, 1115.

(24) Strandberg, R. *Acta Chem. Scand., Ser. A.* **1975**, *29*, 350.

Table 1. Computed Angles (in deg) and Interatomic Distances (in Å) for a Series of Fully Oxidized α- and *β*-Wells−Dawson Anions[a]

anion	symmetry	M_c-O_{term}	M_c-O_{b1}	M_c-O_{b2}	M_b-O_{b2}	M_c-M_c	M_b-M_b[b]	$M_b-O_{b3}-M_b$
α-P_2W_{18}	D_{3h}	1.74−1.75	1.94	1.90	1.95	3.42	3.70 3.76	163
β-P_2W_{18}	C_{3v}	1.74−1.75	1.94	1.90	1.95	3.41−3.42	3.69−3.74 3.78	166
α-P_2Mo_{18}	D_3	1.74	1.89−2.04	1.84−2.05	1.85−2.12	3.46	3.42−3.74 3.89	163
β-P_2Mo_{18}	C_3[c]	1.74−1.75	1.88−2.05	1.84−2.05	1.86−2.12	3.45−3.47	3.40−3.78 3.88	167−169
α-$P_2W_{15}V_3$	C_{3v}	1.76−1.77 (W) 1.65 (V)	1.96 (W) 1.85 (V)	1.89 (W) 1.98 (V)	2.01 (W) 1.84 (V)	3.46 (W) 3.24 (V)	3.62−3.73 3.84	164
β-$P_2W_{15}V_3$	C_{3v}	1.76−1.77 (W) 1.65 (V)	1.96 (W) 1.84 (V)	1.89 (W) 1.98 (V)	2.01 (W) 1.84 (V)	3.46 (W) 3.25 (V)	3.31−3.41 3.85	168

[a] See Figure 1 for the notation of metal and oxygen sites. [b] First values concern two metals on the same belt, whereas the second number is the distance between two metals of different belts. [c] *β*-P_2Mo_{18} was optimized without symmetry constraints.

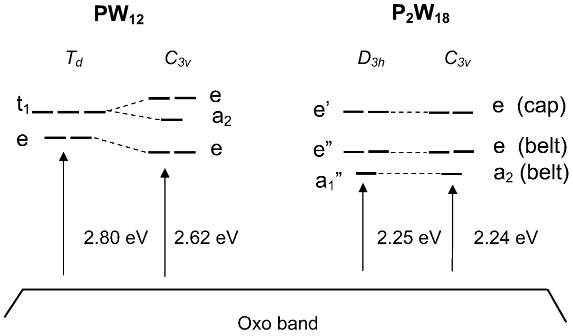

Figure 2. Relative energies of the lowest metallic orbitals of the α and *β* isomers of PW_{12} and P_2W_{18} anions.

appears to be always ~5° bigger in the *β* form. The substitution of three tungsten atoms by vanadiums in one of the polar triads induces some structural changes restricted to the replaced octahedrons. Typically, all the V−O bonds are shorter than the homologous W−O. The V−V distances in the replaced triad are also shorter (3.24 Å) than the typical W···W separation (3.42 Å).

In the absence of paramagnetic ions, fully oxidized heteropolyanions in general, and WD anions in particular, have a simple electronic structure in which the oxo band and the unoccupied set of d_{xy} metal orbitals are perfectly separated.[18] Figure 2 shows a correlation diagram of the frontier orbitals for the most and least symmetric PW_{12} and P_2W_{18} isomers. The frontier orbitals e and t_1 (LUMO and LUMO+1, respectively) of the α-Keggin split into e and e + a_2 after one W_3O_{13} triad is rotated in the T_d structure to give the *β* isomer. Mixing the orbitals of the same symmetry leads to a decrease in the HOMO−LUMO (H−L) gap from 2.80 eV in the T_d geometry to 2.62 eV in the C_{3v} geometry. Consequently, the *β* forms are always more easily reduced than the corresponding α forms. The formal substitution of three octahedrons in α-XM_{12} anions by a XM_9 unit (to give the WD anion) breaks the equivalence of all metals and two types of metal ions appear in an α-X_2M_{18} framework. Cap and belt metals do not participate in the lowest unoccupied orbitals equally. Whereas the d_{xy} orbitals centered on the twelve *belt* metals are the major contributors to the LUMO (a_1'') and LUMO+1 (e''), the LUMO+2 (e') is mainly composed of d_{xy} orbitals centered on the six cap metals. According to this orbital composition, the first reduction in the WD anions takes place in the belt region. A 3D representation of the LUMO is given in Figure 3. Calculations carried out for α-P_2W_{18} of symmetry D_{3h} showed that the reduction at the cap sites—addition of one electron to the LUMO+2 (e')—requires 0.84 eV more than the reduction at the belt sites—addition of one electron to the LUMO (a_1'').[10] The spin polarization data confirm that the first metallic electron is delocalized over the *belt* metal centers. For the 2-fold-reduced species, both the high- and low-spin electronic configurations were computed. In α-P_2W_{18}, the closed-shell configuration $(a_1'')^2\ (e'')^0$ (see Figure 2) was found to be 4.0 kcal mol^{-1} more stable than the triplet state $(a_1'')^1\ (e'')^1$, which was determined by allowing Jahn−Teller relaxation. The singlet open-shell broken symmetry solution was not found to be competitive with the diamagnetic ground state, because the triplet and singlet open-shell states are almost degenerate ($\Delta E_{T-S} = -661$ cm^{-1}). These results agree with the lack of ESR signal for the two-electron-reduced species.[8c] It is well-established that Keggin anions and related structures with an even number of delocalized electrons have a diamagnetic behavior. Although it was initially attributed to a strong antiferromagnetic coupling via a multiroute superexchange mechanism,[19] recent theoretical studies have shown that electron repulsion and electron delocalization can also stabilize the singlet ground state.[20] The theoretical analysis of the coupling of delocalized electrons is a sophisticated problem that, in the case of large systems such as POMs, will still need some time to have concluding results.

The diagram in Figure 2 shows that the energy and composition of WD anion frontier orbitals do not change significantly when one of the cap triads is rotated, and therefore, the redox properties of *β*-P_2W_{18} are expected to be similar to those of the α isomer. By studying the reduced species, we can confirm the predictions made from molecular orbital analysis of the oxidized anions. If *n* is the number of blue electrons in the lowest metallic orbital (a_1'' and a_2 for the D_{3h} and C_{3v} isomers, respectively), the energy difference between the isomers hardly changes with *n*. The magnitude $\Delta E_{\beta-\alpha}$ is 1.83 kcal mol^{-1} for $n = 0$ and decreases by only 0.13 kcal mol^{-1} for $n = 1$ and 0.72 kcal mol^{-1} for $n = 2$. These positive values for $\Delta E_{\beta-\alpha}$ clearly indicate that the α isomer is the most stable, but the difference in stability between the two isomers is quite small. The relative

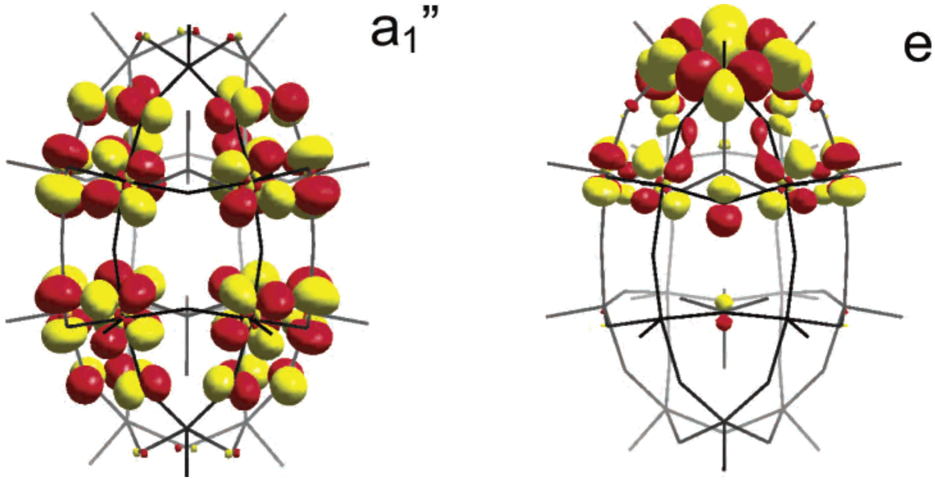

Figure 3. 3D representations for the LUMO of α-$[P_2W_{18}O_{62}]^{6-}$ (orbital of a_1'' symmetry delocalized over the belt metal atoms) and α-$[P_2V_5W_{15}O_{62}]^{9-}$ (one of the components of the e symmetry orbital centered at the vanadium cap ions).

thermodynamic stabilities of the α and β isomers of $[P_2W_{18}O_{62}]^{6-}$ were recently established both in solid state by differential scanning calorimetry and in solution by ^{31}P NMR.[21] Both techniques give the result that the α isomer is more stable than the β one by ∼4 kcal mol^{-1}. Taking into account that the theoretical calculations were carried out with the isolated anions, the agreement between experimental and theoretical results can be considered excellent.

It is well-known that 2:18 molybdates have a specific structure. Whereas the α-P_2W_{18} anion has D_{3h} symmetry, the homologous molybdate is formed of three interpenetrating loops of alternately long and short Mo−O bonds. This distortion confers chirality to the anion, the symmetry of which being D_3. The D_3 geometry was computed to be 7.4 kcal mol^{-1} more stable than the D_{3h} one. Experimental evidence about the chiral structure was obtained from ^{17}O NMR,[22] IR spectroscopy, and optical rotatory dispersion[23] measurements. The bridging molybdenum−oxygen bonds computed for the D_3 geometry are between 1.84 and 2.12 Å, values that are in close agreement with the X-ray data available (1.8−2.1 Å).[24] On the other hand, the Mo−O$_{term}$ distances and all the angles are very close to those of tungstates. To our knowledge, there is no experimental evidence about the shape of the β isomer of the 2:18 molybdate. Perhaps the most significant data concern its reduction properties, which are quite similar to those of the α counterpart.[8b] For the β isomer, two structures were explored: a nondistorted C_{3v} structure, similar to the one optimized for β-P_2W_{18}, and a structure with alternate Mo−O bonds of C_3 symmetry (Figure 4). Considerable computational effort was made to optimize the latter, because the C_3 point group is not available in the ADF package, and the geometry had to be optimized without symmetry constraints. As in the α isomer, the structure with an alternate arrangement of the Mo−O bonds is clearly more stable than the most symmetric form. The energy difference between the C_3 and C_{3v} structures is 8.2 kcal mol^{-1}. Like in the α isomer, the Mo−O distances in the C_3 structure range between 1.83 and 2.12 Å. These relatively important energy differences strongly suggest that the two α and β forms of P_2Mo_{18} have similar structures, with series of short and long Mo−O bonds. We looked for a possible chiral structure for the α-2:18 tungstate; however, the optimization procedure always yields the most symmetric D_{3h} form. This finding seems in agreement with the observation of chiral structures only in molybdates.[23]

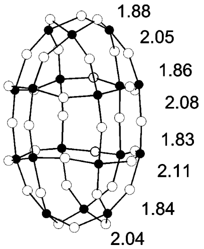

Figure 4. Ball-and-stick view of the DFT-computed geometry of the β-P_2-Mo_{18} anion with formal C_3 symmetry. White and black spheres represent oxygen and molybdenum atoms, respectively. The two internal PO_4 units, as well as the terminal oxygens, are not included for clarity. The distances highlight the alternative disposition of long and short Mo−O bonds forming three interpenetrating loops.

If a more electronegative ion, like V^{5+}, is incorporated into a polar site, there is an inversion of the traditional belt/cap site reduction order. We analyzed the effect that the reduction may have on the equilibrium of the α/β-$P_2W_{15}V_3$ species, where the three Vs occupy three sites in the same triad (shaded octahedrons in Figure 1). The substitution of W by the more electronegative V inverts the order of belt/cap d_{xy}-like orbitals, and then the LUMO in $P_2W_{15}V_3$ is an orbital of e symmetry mainly centered on the three equivalent vanadium atoms[25] (60% V orbitals − 10% belt W orbitals, Figure 3). The LUMO+1 is composed of 65% belt tungsten orbitals and the LUMO+2 of 48% belt W and 10% V orbitals. The shape and energy of the β form orbitals resemble those of the α form orbitals. The H−L gap is similar in both structures. This is important because, although the substitution reduces a metal ion directly involved in the rotation, it does not significantly alter the α/β equilibrium in WD anions. As the values in Table 2 show, the computed $\Delta E_{\beta-\alpha}$ are only slightly higher than those found for the

---

(25) Harmalker, S. P.; Pope, M. T. *J. Am. Chem. Soc.* **1981**, *103*, 7381−7383.

Table 2. Experimental Reduction Potentials and Calculated Relative Stabilities for Several Heteropolyanions

compound	reduction potentials[a] (in V) α	β	$\Delta V_{\beta-\alpha}$	ref
Keggin				
AlW_{12}	−0.62 (1)	−0.45 (1)	−0.17	6
SiW_{12}	−0.26 (1)	−0.14 (1)	−0.12	6
PMo_{12}	+0.36 (2)	+0.55 (2)	−0.19	4
Wells−Dawson				
P_2W_{18}	+0.045 (1)	+0.059 (1)	−0.014	8a
P_2Mo_{18}	+0.46 (2)	+0.53 (2)	−0.07	8b

compound	$\Delta E_{\beta-\alpha}$ (in kcal mol^{-1})[b] $n = 0$[c]	$n = 1$[c]	$n = 2$[c]	ref
Keggin				
PW_{12}	+6.46	+3.00	+0.92	1
SiW_{12}	+6.00	+2.54	−3.30	1
PMo_{12}	+4.84	+1.49	−2.59	1
Wells−Dawson				
P_2W_{18}	+1.83	+1.70	+1.11	this work
P_2Mo_{18}	+2.92		+0.60	this work
$P_2W_{15}V_3$	+2.54	+2.03	+2.31	this work

[a] Values in parentheses are the number of metallic electrons added in each process. [b] Positive values for $\Delta E_{\beta-\alpha}$ mean that the α isomer is the most stable. [c] Number of metal or blue electrons in the framework.

nonsubstituted P_2W_{18} cluster. Moreover, the effect of the single reduction on the α/β equilibrium in $P_2W_{15}V_3$ does not exceed 0.5 kcal mol^{-1}.

For the α/β equilibrium in 2:18 molybdates, we found an energy difference of 2.9 kcal mol^{-1} between the fully oxidized forms. This is smaller than the difference computed for PMo_{12} (4.8 kcal mol^{-1}) and PW_{12} (6.5 kcal mol^{-1}) but somewhat larger than the one found for P_2W_{18} (1.8 kcal mol^{-1}). The LUMO in the chiral α (D_3) isomer of P_2Mo_{18} is 1.86 eV above the oxygen band. The 60° rotation of one capping triad decreases the energy of the LUMO by 0.17 eV, whereas the same transformation in the D_{3h} structure of P_2W_{18} reduces the stabilization of the LUMO to a mere 0.01 eV. This reduction favors the stability of the β form. Hence, after the second reduction, the C_3 structure is only 0.60 kcal mol^{-1} less stable than the D_3 one. The relative stability of α and β isomers fully agrees with the reduction potentials given in Table 2. In general, the β isomers reduce at more positive potentials than the α counterparts, and this behavior is much more significant in the most symmetric Keggin frameworks than in the WD anions. For these latter anions, the polarographic data suggest that the gain in stability of the β form due to the reduction is somewhat larger for molybdates than tungstates.[8]

Conclusions

DFT calculations carried out on Wells−Dawson 2:18 tungstates and molybdates and 2:3:15 vanadotungstates showed that the most symmetric α isomers are slightly more stable than the corresponding β isomers. In contrast to the behavior found for the Keggin anions, the decrease in symmetry when going from the α to the β isomer does not cause any significant decrease in the lowest unoccupied metallic orbitals. Thus, the reduction stabilizes the β form but to a lesser extent than in the Keggin structures. In both forms, the *blue* electrons go to orbitals that are delocalized over metal centers at the equatorial sites. The reduction at the cap centers is possible if one or more cap W(VI) ion in P_2W_{18} is substituted by the more electronegative V(V) ion. This change, however, does not significantly alter the relative stability of α/β isomers.

The present calculations strongly suggest that the β-P_2Mo_{18} anion might have, as the α isomer, a structure with alternately short and long Mo−O bonds. P_2Mo_{18} is the WD anion in which the β form gains more stability by incorporating electrons into its metallic band.

Acknowledgment. We thank the DGICYT of the Government of Spain (grant no. BQU2002-04110-C02-01) and the CIRIT of Generalitat of Catalunya (grant no. SGR01-00315) for support.

IC0262280