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A reinvestigation of isomerism in the Dawson structure: syntheses and ^{183}W NMR structural characterization of three new polyoxotungstates $[X_2W_{18}O_{62}]^{6-}$ ($X=P^V$, As^V)

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Abstract

Three new Dawson-type heteropolyoxotungstates β- and γ-$[As_2W_{18}O_{62}]^{6-}$ and γ-$[P_2W_{18}O_{62}]^{6-}$ have been prepared and identified. A comparative study of these three compounds and of the four other already known $[X_2W_{18}O_{62}]^{6-}$ anions (α and β for $X=P^V$, and α and γ^* for $X=As^V$) has been performed by spectroscopic (IR, Raman, UV–Vis, ^{183}W and, eventually, ^{31}P NMR), polarographic and kinetic measurements, and some erroneous literature assignments have been rectified. The stabilities of the different isomers are discussed in relation with their conditions of formation: the isomerization proceeds along the path $\gamma \rightarrow \beta \rightarrow \alpha$; the relatively high stability of the γ^* anion is also discussed on the basis of the geometrical features of the α- and β-XW_9 half-anion. A rational nomenclature is proposed for the staggered belt junction with respect to the eclipsed one by adding a star, as in $\gamma^*-[As_2W_{18}O_{62}]^{6-}$. ^{183}W solution NMR easily distinguishes α-XW_9 ($\Delta\delta$ about 40 ppm for $X=P$ and 20 ppm for $X=As$; ^2J(W–W) greater than 21 Hz) and β-XW_9 ($\Delta\delta$ about 80 ppm for $X=P$ and 55 ppm for $X=As$; ^2J(W–W) less than 21 Hz).

Introduction

Among the six isomers postulated by Baker and Figgis [1] for the $[X_2W_{18}O_{62}]^{6-}$ anion ($X=As^V$, P^V; $M=Mo^{VI}$, W^{VI}) only two were known at that time: the α isomer known in all cases, whose structure was solved by Dawson [2] in 1953 by an X-ray crystallographic determination on $K_6P_2W_{18}O_{62}\cdot 14H_2O$, and the β isomer $[P_2W_{18}O_{62}]^{6-}$, which was first isolated by Wu [3]. The geometrical structure for this β isomer was initially incorrectly derived from an X-ray diffraction study [4] and shortly after inferred from ^{31}P and ^{183}W NMR solution studies [5, 6], both techniques which have been proved especially suitable for solving such structural problems [7].

The formation of $[X_2Mo_{18}O_{62}]^{6-}$ isomers was proved by one of us [8] and more recently we shortly reported the existence of three new $[As_2W_{18}O_{62}]^{6-}$ isomers [9, 10]. Independently Acerete *et al.* [11] isolated one of these later compounds and from ^{183}W NMR only they assigned it the γ structural arrangement. Some years after Neubert and Fuchs [12] solved by X-ray diffraction the structure of the α and γ^* isomers (*vide infra* for the nomenclature); we will show later in this paper that both Acerete's γ and Fuchs's γ^* anions are in fact the same species.

The Dawson anion is built up from two A-α-XW_9O_{34} half units [13] joined by six common oxygen atoms, lying on a plane of symmetry; the whole anion belongs to D_{3h} point group. The β anion derives from the α isomer by a formal rotation by $\pi/3$ of a polar (cap) W_3O_{13} group: the symmetry is lowered to C_{3v}. The formal rotation by $\pi/3$ of the second polar W_3O_{13} group restores the plane of symmetry and the point group D_{3h} for the γ isomer. In all these anions the hexagonal belts of both XW_9 moieties are symmetry related through the equatorial horizontal plane and their twelve tungsten atoms appear eclipsed along the direction of the C_3 axis.

If the two A-α-WX_9O_{34} subunits are related through an inversion center, as postulated by Wells [14] in 1945 for $P_2W_{18}O_{62}$, the resulting anion named α^* would belong to the D_{3d} point group. Rotation of one or both polar (cap) W_3O_{13} group of this α^* anion would generate the two remaining isomers, $\beta^*(C_{3v})$ and $\gamma^*(D_{3d})$, respectively (Fig. 1). In that case the hexagonal belts of both XW_9 moieties are symmetry related through the center and their twelve tungsten atoms appear staggered along the direction of the C_3 axis.

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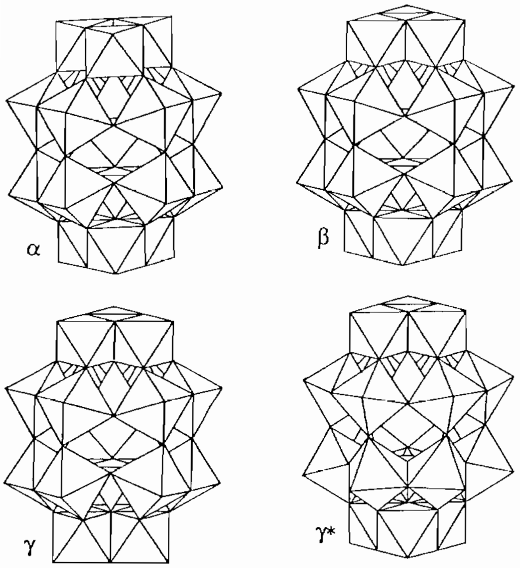


Fig. 1. Schematic polyhedral representation of the α, β, γ and γ* isomers of the Dawson anion.

In the present paper we report the rational preparation of three new compounds, β- and γ-$K_6As_2W_{18}O_{62}$ and γ-$(NH_4)_6P_2W_{18}O_{62}$, and a comparative study with various physicochemical techniques, in particular by vibrational spectroscopy and by NMR (^{183}W and ^{31}P), of all the hitherto known $[X_2W_{18}O_{62}]^{6-}$ anions, with the aim of bringing some clarity to the problem of isomerism in the Dawson structures.

Experimental

Preparations

The α and β octadecatungstodiphosphates were prepared as described in the literature [3, 15].

α-$[P_2W_{18}O_{62}]^{6-}$ Raman (aqueous solution): 1021 (sh), 993 (vs,p), 970 (m), 931 (w), 918 (sh), 875 (w), 618 (w,p) 530 (w), 364 (w), 262 (mw), 226 (m), 202 (m), 173 (m,p), 156, 141, 120 (s,p), 104, 85, 69. IR (NH_4^+ salt, KBr pellet): 1092 (s), 1020 (w), 960 (s), 917 (s), 780 (vs), 600 (vw), 568 (vw), 531 (w), 476 (vw), 374 (ms), 328 (m).

β-$[P_2W_{18}O_{62}]^{6-}$ Raman (aqueous solution): 1018 (sh), 993 (vs,p), 968 (m), 927 (w), 878 (w), 626 (m), 536 (w), 260 (mw), 225 (m), 210 (p), 167 (m), 148, 112 (s,p), 98 (sh), 72. IR (NH_4^+ salt, KBr pellet): 1090 (s), 1024 (sh), 960 (s), 922 (s), 843 (sh), 794 (vs), 597 (w), 568 (vw), 531 (w), 483 (vw), 471 (vw), 400 (sh), 374 (m), 340 (ms).

γ-$(NH_4)_6P_2W_{18}O_{62}\cdot 10H_2O$

In 380 ml of water were dissolved 120 g (25 mmol) of β-$(NH_4)_6P_2W_{18}O_{62}\cdot 16H_2O$. Whilst stirring 32 g (0.3 mol) of sodium carbonate were added. The suspension was stirred for 10 min, then 50 ml (*c.* 0.6 mol) of concentrated hydrochloric acid were added. After complete carbon dioxide escape, 70 g (1.33 mol) of ammonium chloride were added. After 15 min the precipitate was filtered off and 35 g of NH_4Cl were added to the filtrate. A possible precipitate was filtered and to the clear solution 20 g of NH_4Cl were added whilst vigorous stirring. The yellow needles that precipitated were collected on a sintered glass frit and air dried. This crude product that contained NH_4Cl as impurities could be recrystallized from the minimum of water. *Anal.* Calc. for $(NH_4)_6P_2W_{18}O_{62}\cdot 10H_2O$: P, 1.33; W, 71.1; H_2O, 3.87; (NH_3+H_2O), 7.24. Found: P, 1.34; W, 71.5; H_2O, 3.82; (NH_3+H_2O), 7.17%. Thermogravimetric analysis exhibits two plateaus, the first between 200 and 300 °C corresponds to the anhydrous ammonium salt, the second above 550 °C has the anhydride composition. Analytical procedures have been described elsewhere [16, 17]. Raman (aqueous solution): 1020 (sh), 993 (vs), 963 (mw), 928 (w), 880 (w), 615 (w), 540 (sh), 262 (m), 224 (m), 200 (m), 185 (m), 160 (ms), 140 (m), 103 (s), 72. IR (NH_4^+ salt, KBr pellet): 1087 (s), 964 (s), 915 (s), 800 (vs), 595 (w), 568 (vw), 532 (m), 474 (vw), 423 (sh), 394 (sh), 366 (m), 335 (ms), 302 (w).

Octadecatungstodiarsenate isomers

To a sample of 220 g of $Na_2WO_4\cdot 2H_2O$ stirred in 300 ml of water were slowly added 100 ml of 4 M hydrochloric acid then 150 ml of concentrated arsenic acid (*c.* 11M). The solution was raised to ebullition for 10 min then quickly cooled to room temperature. The volume was adjusted to 700 ml with water. The addition of ammonium chloride was fractionated in three steps to partly separate the isomers. The first addition of 50 g of ammonium chloride gave the precipitate **A** (48 g, 26%) that was filtered off. The second addition of 50 g of ammonium chloride gave the main precipitate **B** that is almost pure α isomer (109 g, 60%). A third addition of 50 g of ammonium chloride to the filtrate gave slowly fine yellow crystalline needles. The solution was cooled in an ice-bath and the needles were filtered off (C: 16 g, 9%).

A was dissolved in 100 ml of water and 12.5 g of solid ammonium chloride were added. The precipitate was collected on a sintered glass frit, dissolved in 100 ml of water and 15 g of solid KCl were added to the solution. The precipitate was recrystallized in the minimum of water. *Anal.* Calc. for $K_6As_2W_{18}O_{62}\cdot 18H_2O$: K, 4.68; W, 66.1; As, 2.99; H_2O, 6.46. Found: K, 4.74; W 66.5; As, 2.97; H_2O, 6.35%.

A is not a pure isomer but a mixture of β and γ*, as shown by ^{183}W NMR. The solubilities of the ammonium salts of the two isomers are not sufficiently different to obtain both isomers pure by fractionated crystallization; only the less soluble one, i.e. γ^* was obtained pure after several crystallizations. To get pure β isomer the ammonium salt **A** was passed through a cation exchange resin in Na^+ form. By slow evaporation of the effluent, γ^* isomer appears as little isolated pale yellow blocks and β isomer as sea urchin-like needles. From 9 g of the initial mixture we could separate manually under a binocular lens 900 mg of pure β isomer. An alternative preparation of the γ^* isomer has been described by Acerete *et al.*, who symbolized it as γ [11].

β-$[As_2W_{18}O_{62}]^{6-}$ Raman (NH_4^+ salt): 998 (vs), 880 (m), 620 (mw), 540 (mw), 225 (ms), 205, 180 (s), 150, 120 (s), 96 (s), 78 (s). IR (NH_4^+ salt, KBr pellet): 973 (ms), 929 (sh), 906 (s), 867 (vs), 780 (vs), 525 (mw), 485 (mw), 444 (w), 388 (sh), 372 (s), 332 (m), 315 (m).

γ^*-$[As_2W_{18}O_{62}]^{6-}$ Raman (NH_4^+ salt): 998 (vs), 879 (m), 542 (mw), 228 (s), 148 (vs), 80 (vs). IR (NH_4^+ salt, KBr pellet): 1020 (w), 978 (s), 908 (m), 865 (vs), 790 (vs), 520 (mw), 478 (mw), 438 (w), 384 (ms), 364 (ms), 330 (s) 305 (m).

B was dissolved in 200 ml of water and left for one day at 5 °C. If a precipitate appeared it was filtered off and the filtrate was treated with 32 g of solid potassium chloride. The precipitate was filtered off then dissolved in 125 ml of hot water and allowed to crystallize. It was pure α isomer. *Anal.* Calc. for $K_6As_2W_{18}O_{62}\cdot 14H_2O$: K, 4.75; W, 67.0; As, 3.04; H_2O 5.10. Found: K, 4.72; W 66.7; As, 3.07; H_2O, 5.07%. Raman (NH_4^+ salt): 998 (vs), 965 (sh), 915 (mw), 875 (mw), 860 (mw), 840 (mw), 615 (mw), 540 (mw), 365 (w), 245 (m), 225 (ms), 205, 183 (m), 160 (sh) 150 (ms), 125 (s), 108 (m), 93 (m), 77 (s). IR (NH_4^+ salt, KBr pellet): 973 (ms), 925 (ms), 895 (ms), 866 (s), 835 (s), 770 (vs), 525 (w), 497 (w), 480 (w), 447 (sh), 428 (w), 372 (s), 321 (m).

C was treated with 15 ml of water and the insoluble part was removed on a paper filter. The filtrate was treated with 3 g of potassium chloride. The precipitate was collected and recrystallized in the minimum of water. The crystals that appeared were pure γ isomer. *Anal.* Calc. for $K_6As_2W_{18}O_{62}\cdot 14H_2O$: K, 4.75; W, 67.0; As, 3.04; H_2O 5.10. Found: K, 4.80; W 68.1; As, 3.06; H_2O, 5.15%. Raman (NH_4^+ salt): 998 (vs), 968 (sh), 935 (vw), 868 (w), 840 (vw), 613 (w), 550 (w), 265 (sh), 230 (s), 180 (s), 155 (m), 115 (s), 95 (s), 82. IR (NH_4^+ salt, KBr pellet): 972 (s), 908 (sh), 866 (vs), 780 (vs), 526 (mw), 486 (mw), 445 (vw), 427 (w), 365 (s), 346 (sh), 324 (m), 300 (sh).

Physical measurements

NMR. The ^{183}W NMR spectra were recorded in a 10 mm o.d. tube on a Bruker WM 250 or on a Bruker AM 500 apparatus operating at 10.4 or 20.8 MHz, respectively. Chemical shifts were measured with reference to an external 2 M Na_2WO_4 solution in alkaline D_2O by using saturated dodecatungstosilicic acid ($H_4SiW_{12}O_{40}$) D_2O solution as a secondary standard ($\delta = -103.8$ ppm).

^{31}P spectra were recorded in a 10 mm o.d. tube on a Bruker WM 250 apparatus operating at 101.2 MHz or in a 5 mm o.d. tube on a Bruker AC 300 apparatus at 121.5 MHz. The ^{31}P chemicals shifts were referenced to external 85% H_3PO_4 by the substitution method.

Raman. Raman spectra were run on a Coderg PH0 or a Jobin-Yvon U_{1000} spectrophotometer equipped with a Spectra Physics or a Coherent Innova argon laser. The power of the incident beam (514.5 nm) was adapted to avoid photoreduction of the samples (200 to less than 20 mW).

Infrared. The IR spectra were obtained from KBr pellets (concentration about 1%) on a Nicolet 550 interferometer.

UV–Vis spectroscopy. UV absorption spectra were recorded on a Perkin-Elmer 555 spectrophotometer in the range 200–700 nm (50–14 kK) using Suprasil® quartz Hellma cells of 1 cm path.

Thermogravimetry (*TG*). Thermogravimetry, used to determine the water and ammonium content, was carried out on a Perkin-Elmer TGA-7 electrobalance, at a heating rate of 5 °C per minute (sample weight about 5 mg).

Results and discussion

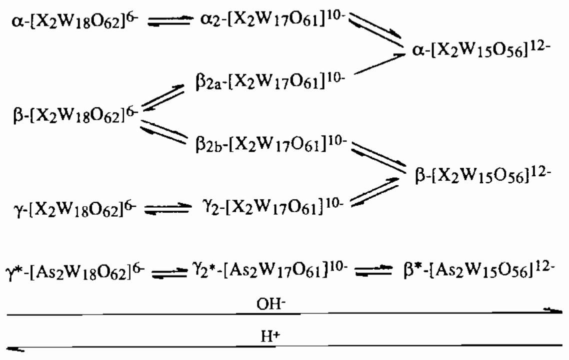
Syntheses

The usual preparation [11, 17, 18] of octadecatungstodiarsenate (abbreviated as As_2W_{18}) is performed by prolonged heating of a mixture of tungstate and arsenic acid. Nevertheless, As_2W_{18} is already partly formed in acidic solutions at ambient temperature. Therefore a few minutes of boiling are sufficient to quantitatively form As_2W_{18} from a mixture of polytungstate and arsenic acid.

$$18[W_7O_{24}]^{6-} + 80H_3AsO_4 \longrightarrow 7[As_2W_{18}O_{62}]^{6-} + 66[H_2AsO_4]^-$$

It is essential to operate with a large excess of arsenic: from a nearly stoichiometric ratio (W/As = 8), Neubert and Fuchs [12] obtained as major product the Keggin anion α-$[AsW_{12}O_{40}]^{3-}$ and very low yields of $[As_2W_{18}O_{62}]^{6-}$ anions (0.4% and 4%).

The solution must be quenched to obtain four isomers by avoiding the isomerization of the less stable ones; they could be separated by selective precipitation using the differences of solubility of their ammonium salts ($\gamma > \alpha > \beta \sim \gamma^*$). The β and γ^* anions are collected simultaneously but the γ^* isomer is easily obtained



Scheme 1.

TABLE 1 Polarographic data for octadecatungstodiarsenates: half-wave potentials (V vs SCE) measured at pH 1 (NaCl 0.9 M, HCl 0.1 M) on a rotating carbon rod electrode (uncertainty 0.02 V)

Anion	$E_{1/2}$ (number of electrons)		
α-$[As_2W_{18}O_{62}]^{6-}$	+0.09 (1)	−0.09 (1)	−0.38 (2)
β-$[As_2W_{18}O_{62}]^{6-}$	+0.12 (1)	−0.06 (1)	−0.35 (2)
γ-$[As_2W_{18}O_{62}]^{6-}$	+0.15 (1)	−0.03 (1)	−0.33 (2)
γ^*-$[As_2W_{18}O_{62}]^{6-}$	+0.12 (1)	−0.06 (2)	−0.35 (2)

The octadecatungstodiphosphates exhibit the same reduction steps, the half-wave potentials $E_{1/2}$ being shifted by about −0.04 V.

pure from the mixture (about 90/10) of the high temperature stable α and γ^* isomers. The β-$[As_2W_{18}O_{62}]^{6-}$ species is then the less accessible one of the four isomers.

On the contrary, the complete formation of P_2W_{18}, from tungstate and phosphoric acid in excess, needs unfortunately several hours of boiling, during which isomerizations could take place and the reaction affords α and β isomers only. To isolate high temperature unstable isomers the only possible route is to use lacunary related compounds as intermediates. Indeed it is now well known [16, 17, 19] that moderate alkalinization of α-X_2W_{18} aqueous solutions induces the departure of one and then of the two remaining tungsten atoms of a W_3O_{13} polar (cap) group, which leads to α_2-X_2W_{17}[†] and α-X_2W_{15}, respectively. From β-P_2W_{18}, because of the non-equivalence of the two PW_9 half-anions, there are two possibilities that leads to: (i) β_{2a}-P_2W_{17} and α-P_2W_{15} if the tungsten atoms depart from the W_3O_{13} group in β-PW_9 or (ii) β_{2b}-P_2W_{17} and β-P_2W_{15} if the departure occurs from the opposite group in α-PW_9 (Scheme 1). Actually a mixture of the two P_2W_{15} isomers has been obtained [16, 19].

Concerning the reverse reaction, i.e. the addition of tungstate to the lacunary compounds, there are in principle two possibilities also for each P_2W_{15}. Actually, the addition of tungstate on α-P_2W_{15} gives only α_2-P_2W_{17} (and α-P_2W_{18}), whereas the addition of tungstate on β-P_2W_{15} gives both β_{2b}- and γ_2-P_2W_{17} (see Scheme 1). Indeed a solution of β-P_2W_{18}, treated with sodium carbonate to get P_2W_{15} and back acidified gives a mixture of three isomers α-, β- and γ-P_2W_{18}, whose ratio has been determined by ^{31}P NMR (*vide infra*).

Electrochemical properties

As in Keggin compounds [20] the $E_{1/2}$ values of the first three waves increases with the number of rotated W_3O_{13} groups (0.04 V per group) and the As_2W_{18} anions are slightly more oxidizing than P_2W_{18} ones (Table 1). The electrochemical reduction in acidic medium has allowed the $[X_2W_{18}O_{62}]^{7-}$ and $[X_2W_{18}O_{62}]^{8-}$ anions to be obtained [21] and has shown that the first two reduction steps are reversible. It is to be noticed that β- and γ^*-As_2W_{18} have the same electrochemical properties and so they are indistinguishable by polarography or electrolysis.

Vibration spectroscopy

As already noted for the Keggin derivatives [22] the vibrational spectra of the polyanions are relatively sensitive to the structural modifications induced by the formal rotation of trimetallic groups. In fact, for each family (P or As), the high frequency modes (stretching of the metal–oxygen double bond and of the XO_4 tetrahedron) [23, 24] in both IR and Raman spectroscopy are nearly independent of the kind of isomer (Figs. 2 and 3). The major differences are observed in the 900 cm^{-1} region, characteristic of the stretchings of the μ-oxo bridges between the different bi- and trimetallic groups, and also in the low-wavenumber part, characteristic of complex modes, involving W–O–W bending and 'skeletal' vibrations: they concern essentially the 300–400 cm^{-1} region of the IR spectra and the very low part (less than 300 cm^{-1}) for the Raman spectra [22]. With the help of polarization measurements, Raman spectroscopy is able to quantify the different isomers, and this technique was actually used throughout to monitor the purification of the $[As_2W_{18}O_{62}]^{6-}$ anions. The useful Raman wavenumbers for this purpose are, for aqueous solutions: α, 183 (p), 128 (p); β, 208 (p), 182 (part p), 121 (p); γ^*, 150 (p).

The γ^*-$[As_2W_{18}O_{62}]^{6-}$ presents, especially in Raman spectroscopy, rather simple spectra, completely different from those published by Neubert and Fuchs [12]; actually our spectra were obtained from rhombohedral crystals whose space group[††] is identical to that of the crystal

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[†] The index 2 indicates, for a monovacant Dawson type compound, a lacuna in a W_3O_{13} polar group.

[††] Francis Robert is greatly acknowledged for the help in determination of the space group

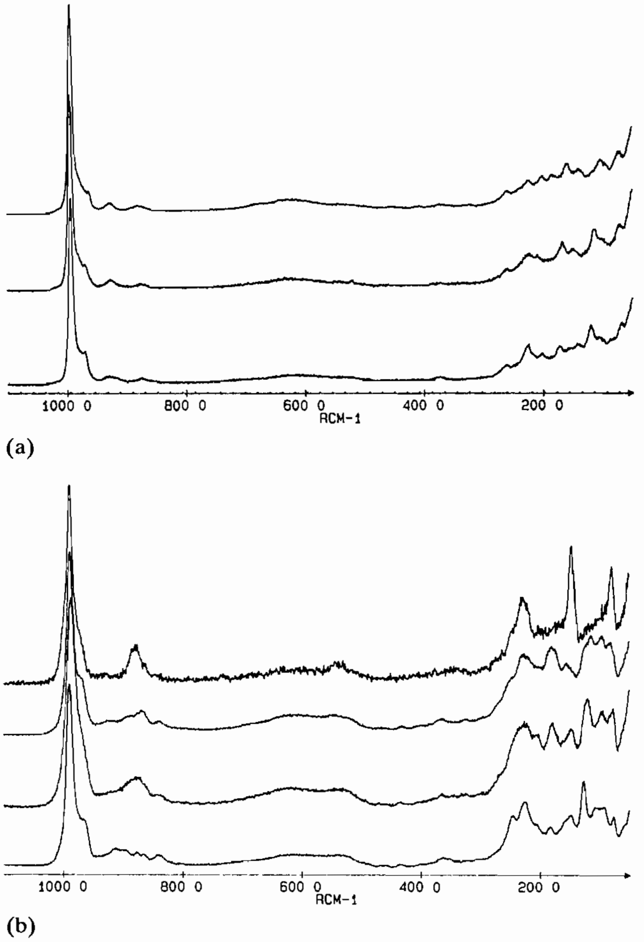


Fig. 2. Raman spectra of all $[X_2W_{18}O_{62}]^{6-}$ anions: (a) from bottom to top, α-, β- and γ-$[P_2W_{18}O_{62}]^{6-}$ in aqueous solution; (b) from bottom to top, α-, β-, γ- and γ*-$[As_2W_{18}O_{62}]^{6-}$ as solid ammonium salts; noisy spectra of both β and γ* anions are due to the very low laser power (less than 20 mW) needed to avoid their photoreduction.

determined by Neubert and Fuchs (called $\beta\beta_2$ by these authors). It is clearly evident, from the broadness of the lines, that the spectra published by Fuchs are spectra of mixtures (impure samples) which perhaps do not even contain the γ* anion.

UV–Vis spectroscopy

The UV spectra are almost independent of the nature of the heteroatom P or As. The α isomers exhibit only shoulders at about 40.8 kK and the γ ones a poorly resolved maximum at 40 kK whereas β and γ* isomers exhibit maximums at 39.3 kK ($\epsilon = 5.15 \times 10^4$ M^{-1} cm^{-1}). The UV spectra of the last ones are indistinguishable. All the spectra exhibit a second shoulder at 33–35 kK and a third one in the near-UV (26–27 kK). In the visible part of the spectra, arsenic compounds absorb slightly more than phosphorus ones and molar absorptivities of the different isomers follow the trend $\alpha < \beta < \gamma < \gamma^*$.

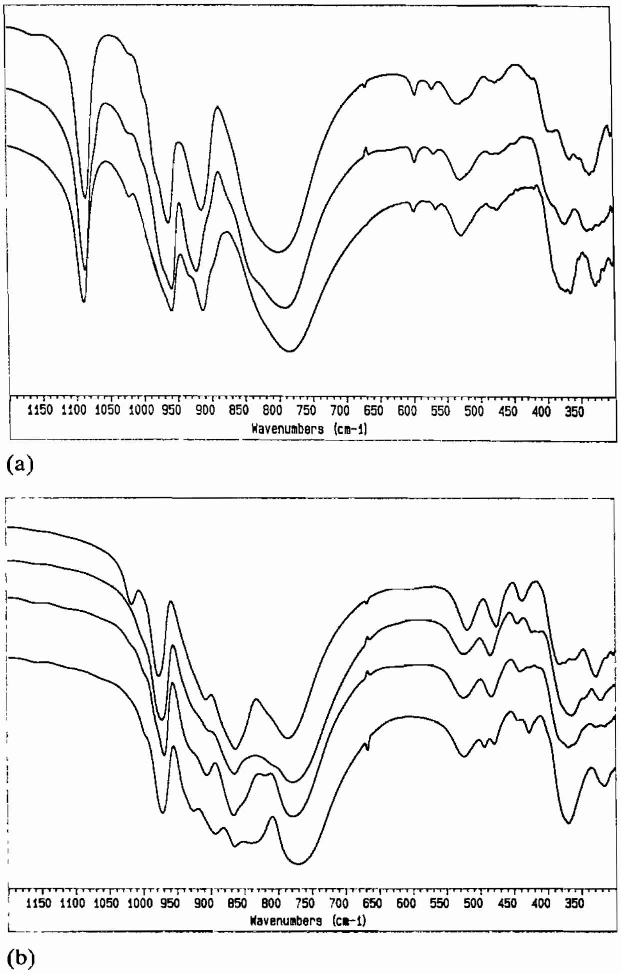


Fig. 3. IR spectra of all $[X_2W_{18}O_{62}]^{6-}$ anions (NH_4^+ salts; KBr pellets): (a) from bottom to top, α-, β- and γ-$[P_2W_{18}O_{62}]^{6-}$; (b) from bottom to top, α-, β-, γ- and γ*-$[As_2W_{18}O_{62}]^{6-}$.

TABLE 2. Decomposition rate constants at 25 °C (pH 5.4: sodium acetate 0.5 M–acetic acid 0.1 M; pH 6.1: sodium acetate 0.97 M–acetic acid 0.04 M)

Anion	k (s^{-1})	
	pH 5.4	pH 6.1
α-$[P_2W_{18}O_{62}]^{6-}$	4.1×10^{-5}	2.5×10^{-4}
β-$[P_2W_{18}O_{62}]^{6-}$	6.2×10^{-5}	2.7×10^{-4}
γ-$[P_2W_{18}O_{62}]^{6-}$	1.1×10^{-4}	4.2×10^{-4}
α-$[As_2W_{18}O_{62}]^{6-}$	1.6×10^{-4}	6.9×10^{-4}
β-$[As_2W_{18}O_{62}]^{6-}$	1.7×10^{-4}	7.3×10^{-4}
γ-$[As_2W_{18}O_{62}]^{6-}$	2.2×10^{-4}	7.8×10^{-4}
γ*-$[As_2W_{18}O_{62}]^{6-}$	4.3×10^{-4}	1.4×10^{-3}

Aqueous solution stabilities

We shall consider the stabilities towards isomerization and the stabilities towards alkaline hydrolysis, with formation of the lacunary compounds X_2W_{17} (Table 2). The latter reaction has been found to be a first order [16] reaction, catalyzed by acids and bases, that depends on the pH, on the nature and the concentration of the buffer and of the counter-ion. The rate follows the trends $K^+ > Na^+ > Li^+$ and $\alpha < \beta < \gamma < \gamma^*$. The P_2W_{18} anions are stable at a higher pH than the As_2W_{18} ones and at pH 5.4 γ^*-As_2W_{18} hydrolyzes twice as fast as γ-As_2W_{18}.

The α isomers are the only species stable in aqueous solution; all the other X_2W_{18} anions described herein isomerize. The most reactive species is γ-P_2W_{18}, whose half-life is some days in acidic solutions and some months in the solid state. The isomerization rates follow the trend γ-$P_2W_{18} > \gamma$-$As_2W_{18} \sim \beta$-$As_2W_{18} > \beta$-$P_2W_{18} >$ γ^*-As_2W_{18}. The two latter species are resistant to several hours of boiling but only γ^*-As_2W_{18} resists at pH>3. However at pH 3.8 it isomerizes to give the α isomer with a half-life of about two years. The isomcrization mechanism is unknown but there are two possible paths: (i) a rotation of the W_3O_{13} group as a whole, that probably does not depend on the pH; (ii) the isomerization as X_2W_{17}; this route depends on the X_2W_{17} isomerization rate and of course on the pH, which controls the X_2W_{17}/X_2W_{18} ratio. This second way is perhaps the only one in the case of γ^*-As_2W_{18}: it would explain at once fast hydrolysis and slow isomerization.

^{31}P *NMR spectroscopy*

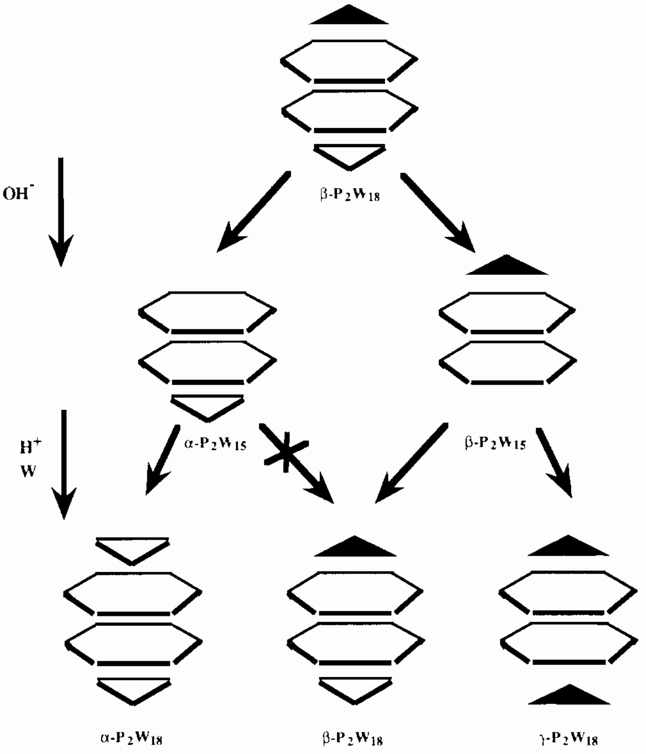
The ^{31}P NMR spectrum of the γ-$[P_2W_{18}O_{62}]^{6-}$ anion exhibits a unique line (−10.5 ppm) shifted by 2 ppm to high frequency with respect to the α isomer (−12.5 ppm); both lines of the β isomer are exactly in between the two previous lines (−11.0 and −11.8 ppm), with the same center of gravity. ^{31}P NMR spectroscopy was the technique used to monitor the synthesis of the γ isomer. It has been shown that alkalinization of β-P_2W_{18} and subsequent acidification leads to a mixture of the three isomers (α less than 60%; β less than 20%; γ about 25%) (see Schemes 1 and 2).

^{183}W *NMR structural characterization*

Phosphorus derivatives

As previously mentioned by Acerete *et al.* [25], α-$[P_2W_{18}O_{62}]^{6-}$ presents two ^{183}W NMR signals in 1/2 ratio at −126.5 and −172 ppm ($\Delta\delta = 45.5$ ppm)[†], respectively, according to the six equivalent cap atoms (polar) and twelve equivalent belt atoms of the Dawson structure (D_{3h} symmetry) (Fig. 4).

The β isomer exhibits four ^{183}W lines in a 1/1/2/2 ratio at −110.6, −129.9, −170.1 and −190 ppm, respectively [6]; this result, in accordance with ^{31}P NMR results [5], allows the structural proposal of Matsumoto and Sasaki [4] based on crystallographic determination to be ruled out. The β anion consists then of two unequivalent PW_9 moieties, i.e. one A-α-PW_9 and one A-β-PW_9. As shown above two anions can be formed with eclipsed ($\alpha\beta$E) or staggered ($\alpha\beta$S) belt junctions, respectively. In fact, the structural hypothesis of an eclipsed belt junction for this anion cannot be ascertained by ^{183}W NMR only, and the chemical properties must be involved to eliminate the other proposal.



Scheme 2
(A black triangle corresponds to a rotated cap group (with respect to the α anion).)

For the β isomer the ^{183}W NMR lines assignment could be made by comparison with that of α-$[P_2W_{18}O_{62}]^{6-}$ (Table 3). Both central lines (−129.9 and −170.1 ppm) with nearly the same chemical shift difference ($\Delta\delta = 40.2$ ppm) and the same tungsten–tungsten couplings (^2J(W–W) = 21 Hz) as for the two lines of the α anion ($\Delta\delta = 45.5$ ppm; ^2J(W–W) = 21.1 Hz) could be assigned to the A-α-PW_9 moiety (Table 3). Then the two border lines (−10.6 and −190 ppm; $\Delta\delta = 79.4$ ppm), with a smaller tungsten–tungsten coupling (^2J(W–W) = 19.2 Hz), are assigned to the A-β-PW_9 moiety[††]. Mention must be made of the interunit

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[†] Our values slightly differ from those of Acerete *et al.* [11], due to some medium effects, but the chemical shift differences $\Delta\delta$ remain the same.

[††] The same trend is actually observed for other polyoxotungstates with A-α- or A-β-PW_9 subunits: ^2J(W–W) tungsten–tungsten coupling is slightly smaller for β- than for α-$SiMo_3W_9$ ((20.3 and 21.3 Hz, respectively). This is in accordance with a more acute μ-oxo bridge angle in the β anions (*c.* 140° in β-SiW_{12} compared with *c.* 150° in α-SiW_{12}).

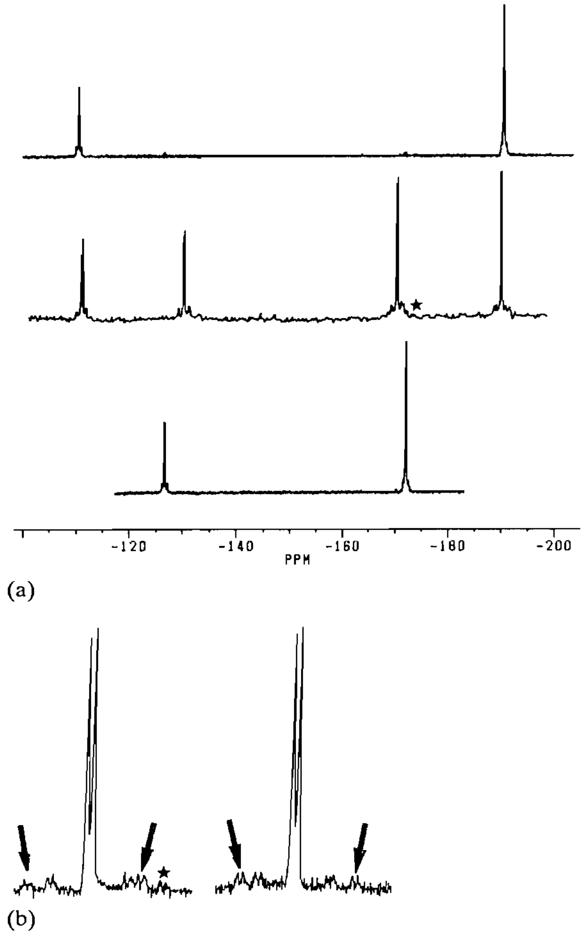

Fig 4 ^{183}W NMR spectra of all $[P_2W_{18}O_{62}]^{6-}$ anions in aqueous solutions: (a) from bottom to top, full spectra of α-, β- and γ-species; (b) expanded part: resonance lines from the belt Ws of the β anion, showing the mutual coupling (31 Hz, AB system, satellites marked by arrows) The * indicate the line of the α-isomer (less than 2% impurity).

belt–belt coupling (^2J(W–W) = 31 Hz), with a slight AB pattern (at 10.4 MHz) for the satellites of the −170.1 and −190 ppm lines (Fig. 4): such a high tungsten–tungsten coupling is consistent with a large angle for the μ-oxo junction between two subunits [26]; although the β anion structure has not been solved by X-ray, it could be anticipated that this angle will not differ strongly from that of the symmetrical α anion 162° [27].

The ^{183}W NMR spectrum of the γ-$[P_2W_{18}O_{62}]^{6-}$ anion exhibits the two lines in 1/2 ratio at −110.4 (6W) and −190.8 (12W) ppm which are expected for a symmetrical anion. The interline separation $\Delta\delta = 80.4$ ppm and the relatively small cap–belt coupling constant (^2J(W–W) = 19.8 Hz) agree with the hypothesis of two A-β-PW$_9$ moieties. In that case too, the chemical properties and the isomerization path (γ→β→α) are required to rule out the γ* (ββS) structure.

Arsenic derivatives

Bearing in mind the previous considerations and assuming the same rules for the arsenate anion, i.e. greater interline separation and weaker cap–belt coupling ^2J(W–W) for the A-β-AsW$_9$ moiety, with respect to the A-α-AsW$_9$ one, the four isomers (Fig. 5) are then A-α-AsW$_9$-A-α-AsW$_9$ (abbrev. αα) for the α anion, αβ for the β one and ββ for both γ and γ* isomers (Table 3). Neubert and Fuchs [12] have solved the structures of α and γ* by X-ray diffraction: actually, α-$[As_2W_{18}O_{62}]^{6-}$ is isostructural with α-$[P_2W_{18}O_{62}]^{6-}$ (ααE configuration) and the γ* isomer has the ββS arrangement, with D_{3d} symmetry. Consequently there is no more ambiguity for the γ isomer, which is necessarily the ββE species (D_{3h} symmetry), but there remains two possibilities for the last β isomer, i.e. αβS or αβE. As there is no apparent reason for assuming an inversion of stability of the staggered/eclipsed XW$_9$ junctions by substituting As for P, the β-$[As_2W_{18}O_{62}]^{6-}$ isomer should be isostructural with the β-$[P_2W_{18}O_{62}]^{6-}$ anion (αβE). This structural assignment is confirmed by the redox potential trend and the observed isomerization sequence γ→β→α, where each step involves only a relatively minor structural modification consisting of a formal cap rotation.

As already discussed, the second isomer prepared (at elevated temperature) and named γ by Acerete *et al.* [11], must be γ*-$[As_2W_{18}O_{62}]^{6-}$ and this can be also demonstrated by ^{183}W NMR: although both ββ anions have very similar NMR spectra, they differ markedly in the cap–belt ^2J(W–W) coupling constant (19.5 and 20.7 Hz, respectively), and the cap–belt Δδ separation (53.8 and 56.3 ppm, respectively). The noisy spectrum of Acerete's species does not allow homonuclear tungsten–tungsten coupling constants to be observed, however the interline separation of 56 ppm clearly demonstrates that this spectrum corresponds to the γ* anion.

Discussion of the NMR parameters

Chemical shifts in ^{183}W NMR are the subject of many speculations and a comprehensive theory is far from being established. Therefore we cannot precisely explain the following observations:

- for the same XW$_9$ moiety, the cap is deshielded with respect to the belt, the cap–belt chemical shift difference being about 30–40 ppm higher in the case of the β half-anion with respect to the α half-anion;
- the cap–belt chemical shift difference is about 20–25 ppm higher for the phosphorus moieties than for the corresponding arsenic ones;
- for each type of half-anion the weighted chemical shift ($\delta_{wt} = 1/3(\delta_{cap} + 2\delta_{belt})$ is about 20 ppm more negative in the case of phosphorus compounds (see Table 3).

TABLE 3. ^{183}W NMR data for all $[X_2W_{18}O_{62}]^{6-}$ anions[a]

Anion	α-XW$_9$ moiety					β-XW$_9$ moiety					belt–belt	
	δ_{cap} (6 or 3W)	δ_{belt} (12 or 6 W)	$\Delta\delta$	^2J(W–W)	$-\delta_{wt}$	δ_{cap} (6 or 3W)	δ_{belt} (12 or 6 W)	$\Delta\delta$	^2J(W–W)	$-\delta_{wt}$	$\Delta\delta$	^2J(W–W)
α-$[P_2W_{18}O_{62}]^{6-}$ $\alpha\alpha$E	−126.5 (1.2)	−172 (1.6)	45.5	21.1	156.8							
β-$[P_2W_{18}O_{62}]^{6-}$ $\alpha\beta$E	−129 9 (1.1)	−170 1 (1.6)	40 2	21	156.7	−110.6 (1.2)	−190 (1.6)	79.4	19.2	163.5	20	31[b]
γ-$[P_2W_{18}O_{62}]^{6-}$ $\beta\beta$E						−110.4 (1.2)	−190 8 (1.7)	80.4	19.8	164.0		
α-$[As_2W_{18}O_{62}]^{6-}$ $\alpha\alpha$E	−120.8	−144 1	23.3	21.4	136.3							
β-$[As_2W_{18}O_{62}]^{6-}$ $\alpha\beta$E	−123.4	−140.6	17.2	21.4[b]	134.9	−106.6	−160 1	53 5	19.5	142.3	20	30.3[b]
γ-$[As_2W_{18}O_{62}]^{6-}$ $\beta\beta$E						−106.3	−160.1	53.8	19.5	142.2		
γ^*-$[As_2W_{18}O_{62}]^{6-}$ $\beta\beta$S						−109.7	−166.0	56.3	20.7	147.2		

[a] Chemical shifts in ppm relative to alkaline 2 M Na_2WO_4 in D_2O Coupling constants ^2J(W–W) in Hz. For the phosphorus anions, the ^2J(W–P) (in Hz) are given in parentheses under the δ value For each half-anion, $\delta_{wt} = 1/3\ (\delta_{cap} + 2\delta_{belt})$. [b] AB system for the tungsten–tungsten satellites at 10 4 MHz.

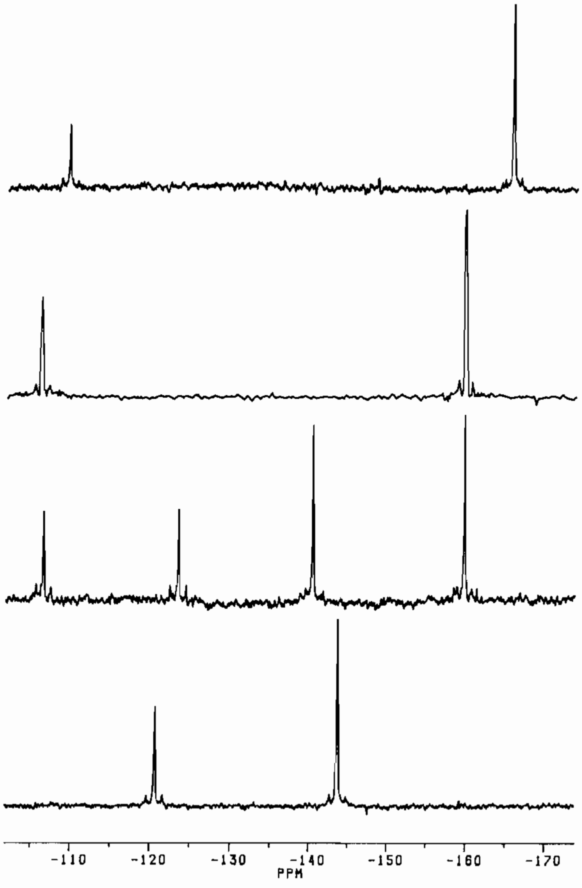

Fig. 5. ^{183}W NMR spectra of all $[As_2W_{18}O_{62}]^{6-}$ anions in aqueous solutions; from bottom to top, α-, β-, γ- and γ^*- species.

In fact the tungsten–tungsten coupling constants ^2J(W–W) are more easily connected to the geometry of the anions: owing to the relatively high symmetry of the compounds, the few observable coupling constants concern junctions between tungsten atoms belonging to adjacent bi- or trimetallic fragments. The widely opened μ-oxo bridge (likely > 160°) of the junction between XW$_9$ half-anions is responsible for the large belt–belt coupling (31 Hz), visible only for the less symmetrical β anions; concerning the cap–belt junction, the small coupling constants for the β half-anions likely correspond to bridge angles significantly smaller than for the α ones: actually the corresponding angle values, recalculated from ref. 12 for α-$[As_2W_{18}O_{62}]^{6-}$ ($\alpha\alpha$E) and γ^*-$[As_2W_{18}O_{62}]^{6-}$ ($\beta\beta$S), are 151.1° (^2J(W–W) = 21.4 Hz) and 149.6° (^2J(W–W) = 20.7 Hz), respectively. For the low cap–belt coupling constants (^2J(W–W) < 20 Hz) observed in all eclipsed structures containing the β-XW$_9$ half anion, the bridge angle in the β half-anion is likely to be even smaller, around 145°.

Conclusions

About the similarity of the β and γ^* isomers

For the different isomers, differences in their electronic properties (electrochemical and UV–Vis absorption) and in their solubility are essentially governed by the relative disposition of the peripheral oxygen atoms. All structures are formally related through the $\pi/3$ rotation over the C_3 axis of either a W_3O_{13} polar group (α to β, β to γ) or a complete XW$_9$ moiety (γ

to γ^*); however the γ^* anion structure can be viewed as deriving from the β one by the $\pi/3$ rotation of one equatorial belt (see Fig. 1); concerning the external oxygen atoms only, this rotation is approximately a symmetry operation for the hexagonal belt (nearly six-fold symmetry) and actually ball models show that the external oxygen atoms occupy nearly the same positions in both γ^* and β isomers. This could explain the great similarity of the electronic properties and of the solubility of these isomers. Of course, if inner atoms are concerned (^{183}W NMR, vibration spectroscopy), these γ^* and β anions can be distinguished as easily as all other isomers.

About the stabilities of the different isomers and the existence of further species

Only two of the six isomers of Baker and Figgis remain yet unknown, i.e. α^* ($\alpha\alpha$S) and β^*($\beta\beta$S) that would both have staggered-belt structures.

Let us consider the hexagonal belt of the α-XW_9 anion: according to the structural determination of d'Amour [27] and of Neubert and Fuchs [12], the six upper oxygen atoms, in common with the trimetallic group, constitute a small hexagon with alternately short and long O–O distances of about 260 pm between oxygens belonging to adjacent bimetallic groups and 315 pm for oxygens in the same bimetallic group. This geometrical arrangement could accommodate the trimetallic group, either with the α junction (short distance corresponding to an octahedron edge in the trimetallic group) or, with more constraint, with the β junction. The lower oxygen atoms of the belt are arranged on a larger hexagon, with a more pronounced distortion (d(O–O) about 310 pm for oxygens in the same bimetallic group and 430 pm in the other case). This bond alternation for the XW_9 half-anion can be maintained in the eclipsed-belt structure, where the bonding oxygens are located in the horizontal plane. On the contrary the staggered-belt junction requires the equalization of all O–O distances in the central hexagon and therefore a rearrangement of the belt: as shown by polyhedral models, in a bimetallic group of the belt, such a rearrangement implies the mutual displacement of the two octahedra with respect to their common edge; lengthening the O–O distances in the lower part results in a shortening in the upper part (Fig. 6).

The O–O bond alternation in the upper hexagon becomes reversed with respect to the previous case, i.e. the shortest O–O bond, about 255 pm [12], is between oxygens belonging to the same bimetallic group, the other one is significantly larger (about 325 pm); such a configuration is favourable, and perhaps possible only for a β junction (Fig. 6). It appears then that the γ^* isomer would be the most stable among the staggered structures and that the isomerization trend would be $\alpha^* \rightarrow \beta^* \rightarrow \gamma^*$. This agrees also with the absence of an observed intermediate in the reaction $\gamma^* \rightarrow \alpha$.

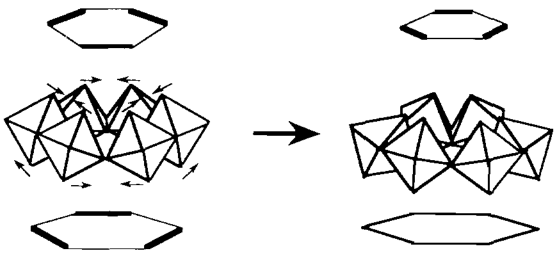

Fig. 6. Distortion of the hexagonal belt, from the eclipsed junction (left) to the staggered junction (right). On the hexagon of oxygen atoms, heavy and thin lines symbolize short and large O–O distances, respectively, full lines stand for the hexagon with all six O–O distances being equal.

About isomers in molybdenum species

If the X_2W_{18} isomerization problem may be considered as solved, it is not the case for the X_2Mo_{18} one. The structure of the α isomer is well known [27, 28]; the second isomer was noted as β [8] because it is more oxidizing than the α isomer; however it was shown by Zugazagoïtia-Herranz [29] that the ^{31}P NMR spectra of reduced forms of this P_2Mo_{18} anion each exhibit a unique line. So it does not agree with a β isomer but with a γ, γ^* or α^*. Taking into account the previous remarks the α^* structure seems unlikely, and a careful study by X-ray diffraction would probably be necessary to choose between γ and γ^*.

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