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Synthesis, Structural Characterization, and Oxidation−Reduction Behavior of the γ-Isomer of the Dodecatungstosilicate Anion

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The reaction of tungstate ions with the γ-10-tungstosilicate in mixed water−ethanol (v/v) yields the corresponding isomer of the 12-tungstosilicate isolated as its tetrabutylammonium salt. It was characterized by means of ^{183}W NMR, infrared, Raman, and UV spectroscopies and was identified with the isomer resulting from the Keggin structure (α-isomer) by rotation of two tritungstic groups by $\pi/3$. Cyclic voltammetry shows that the reducibility increases in the sequence $\alpha-\beta-\gamma$ as the number of rotated tritungstic groups. Whereas the γ-12-tungstosilicate anion is unstable in pure aqueous solution whatever the pH value, it is stable in mixed aqueous−organic or pure organic solvents, even at boiling temperatures. In contrast, the two- and four-electron-reduced blue species are stable in aqueous media but not the one-electron-reduced blue. Study of the ^{183}W NMR spectrum of the two-electron-reduced species showed that the two spin-paired electrons are delocalized on all the W atoms on the NMR time scale but have a larger residency time on one group of four atoms.

Introduction

Among the five $[XM_{12}O_{40}]^{n-}$ isomers postulated by Baker and Figgis,[1] two have been reported for M = Mo^{VI} and W^{VI}. The former, α-isomer, has the well-known Keggin structure[2] built from corner-sharing trimetallic fragments according to a T_d symmetry. The latter, β-isomer, is structurally related to the previous one by the formal rotation of one trimetallic group by 60° about its C_3 axis, resulting in a C_{3v} symmetry. A specific synthesis for the β-isomer of the dodecatungstosilicate anion has been reported[3] and its structure determined by X-ray analysis.[4,5] This isomer is very stable in aqueous solution, even at boiling temperatures, in contrast to the analogous molybdic compounds, for which a transformation $\beta \rightarrow \alpha$ was observed.[6]

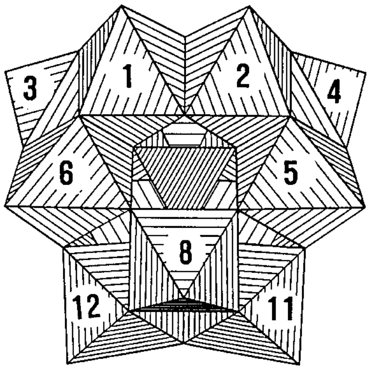

Figure 1. Polyhedric structure of the γ-isomer of the dodecatungstosilicate anion.

The γ-isomer (C_{2v} symmetry), where two metallic groups are rotated (Figure 1), had not been obtained until now. The so-called γ-dodecatungstophosphate reported by Fuchs[7] was proved to be a structurally disordered α-isomer.[8] Only the corresponding divacant anion $[XW_{10}O_{36}]^{n-}$ has been prepared with X = P^{V} [9] and Si^{IV} [10] and X-ray-investigated. The divanadium complexes γ-$[XV_2W_{10}O_{40}]^{n-}$ have been obtained from these species and were proved to be stable in nonaqueous solvents but to slowly isomerize in aqueous solution, leading to various β-isomers depending on the pH values.[11,12] The same behavior was observed when the two vanadium atoms were in oxidation state IV; the presence of a bis(μ-oxo) junction between the two vanadium atoms in this complex leads to an unstable structure in aqueous solution. A different behavior was observed when $[Mo_2O_4(H_2O)_6]^{2+}$ was added to $[SiW_{10}O_{36}]$,$^{8-}$, leading to a stable binuclear complex of Mo(V) in aqueous solution.[14] We were interested in studying the influence of the oxidation state of some tungsten atoms, VI or V, on the stability of the γ-isomer. Moreover, it is well-known that the electrons in polyoxotungstic species are delocalized over numerous tungsten atoms at room temperature, involving a rapid thermal hopping of those electrons among tungsten atoms.[14] The electrons are delocalized among the 12 equivalent W atoms in the α Keggin structure,[15] but only among the 12 belt atoms of the 18 total W atoms in the 18-tungsto α Wells−Dawson structure, in which there are two types of tungsten atoms.[16] Since there are four types of nonequivalent tungsten atoms expected in the γ

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structure, we wished to learn whether the structural changes resulting from the rotation of two trioxotungstic groups lead to a strong localization of the electrons on certain tungsten atoms.

In this paper, we report the synthesis of the γ-dodecatungstosilicate anion and its stability in solution. Its electrochemical behavior and properties of the reduced derivatives are compared to those of the α- and β-isomers.

Experimental Section

Preparation. The solution of the γ-$[SiW_{12}O_{40}]^{4-}$ anion was obtained in mixed v/v water–ethanol solvent by addition of sodium tungstate to a solution of the potassium γ-decatungstosilicate salt in a ratio of 2:1 and in the presence of HCl (0.5 mol·L^{-1}). Preparation of the tetrabutylammonium salt was previously reported in Inorganic Syntheses series.[17]

Electrochemical Reduction. Electrochemical reductions were carried out on a mercury cathode by electrolysis at a controlled potential in acetonitrile for the tetrabutylammonium salt or in the mixed water–ethanol solution of γ-$[SiW_{12}O_{40}]^{4-}$ with an acetic acid buffer for alkali salts. Cesium salts of the 2e- or 4e-reduced derivatives were obtained by addition of solid CsCl to their solutions.

Characterization. The polyanion was characterized by electronic, infrared, and Raman spectroscopies, by ^{183}W NMR, and by voltammetry. NMR spectra were recorded on a Bruker WM 250 spectrometer operating at 10.4 MHz, from dimethylformamide solutions of the tetrabutylammonium salt for the oxidized species or from aqueous solutions of the two-electron-reduced blue derivative. Chemical shifts are referenced to external Na_2WO_4 in alkaline D_2O.

Results and Discussion

Synthesis. The divacant $[HSiW_{10}O_{36}]^{7-}$ polyanion was, *a priori,* a suitable species from which to synthesize polyanions of the type γ-$[SiW_{10}M_2O_{40}]^{n-}$. Such polyanions have been effectively obtained with metals in oxidation state V (vanadium[11] and molybdenum[12]) and slowly isomerize (vanadium) or are stable (molybdenum) in aqueous solution depending on the pH value. The reaction of tungstate(VI) with the γ-decatungstosilicate anion was studied in concentrated aqueous solution at pH 2–3 and was monitored by Raman spectroscopy. The variation of the intensity of the band near 1000 cm^{-1}, characteristic of complete tungstosilicic Keggin-like structures, clearly indicated the formation of an addition compound involving two tungsten atoms per polyanion. The Raman spectrum of the solution slowly changed with time, showing that the initial species was not stable in aqueous solution. After 2 days, a Raman spectrum and a polarogram of the solution showed that only the β-isomer of $[SiW_{12}O_{40}]^{4-}$ was present. It was observed that the initial compound formed by reaction of tungstate with the γ-decatungstosilicate was stabilized by addition of a nonaqueous solvent such as ethanol or dioxane; hence, it was synthesized in a 1:1 water–ethanol mixture and precipitated by addition of tetrabutylammonium bromide. This salt is soluble in numerous organic solvents, and analysis agrees with the formula $[(C_4H_9)_4N]_4[SiW_{12}O_{40}]$.

^{183}W NMR spectrum. The spectrum of the dimethylformamide solution (Figure 2) exhibits four lines denoted as A, B, C, and D from low to high fields, with a 2:1:2:1 intensity ratio, respectively. The chemical shifts and coupling constants are as follows: (A) −104.7 ppm ($^2J_{W-W}$ = 22.Hz, AB pattern, and 6 Hz); (B) −116.8 ppm, ($^2J_{W-W}$ = 22 Hz, AB pattern, and 7 Hz); (C) −127.4 ppm ($^2J_{W-W}$ = 21 Hz and 7 Hz); (D) −160.1 ppm ($^2J_{W-W}$ = 7 Hz). It does not correspond to a fortuitous mixture of α- (one line at −92.1 ppm) and β-isomers (three lines at −103.5, −104.0, and −120.5 ppm with intensity ratio 1:2:1) but agrees with a γ-isomer where the tungsten multiplicities are 2:4:2:4 in increasing order of tungsten atom numbering (Figure 1).

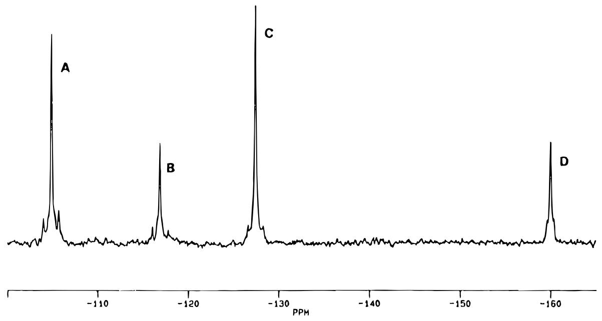

Figure 2. ^{183}W NMR spectrum of the γ-$[SiW_{12}O_{40}]^{4-}$ anion, as the tetrabutylammonium salt in dimethylformamide solution.

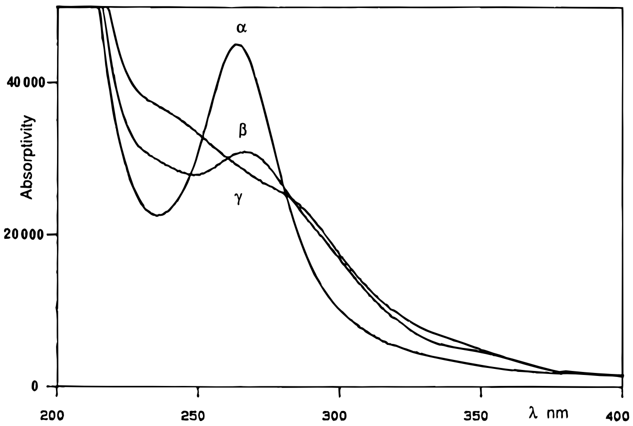

Figure 3. Ultraviolet electronic spectra of the three isomers of $[SiW_{12}O_{40}]^{4-}$ (solutions of the tetrabutylammonium salts in acetonitrile).

Weak couplings, less than 10 Hz, are expected for the edge junctions and strong couplings, about 20 Hz, for the corner μ-oxo junctions. Among the two lines of multiplicity 1, the higher field one D, without strong coupling, is assigned to the bis(μ-oxo)-bridged W_1 and W_2 tungsten atoms hereafter denoted W_d and line B should arise from the W_7 and W_8 tungsten atoms (W_b), belonging to unrotated trimetallic groups. The low-field line A presents two pairs of degenerated strong-coupling tungsten satellites and is related to the W_3–W_4–W_5–W_6 atoms (W_a). Therefore, the remaining resonance C with a less intense strong coupling is assigned to the equivalent W_9–W_{10}–W_{11} and W_{12} atoms (W_c). Irrespective of the concentration, the high-field line D is broader than the three other lines, indicating a smaller spin–spin relaxation time T_2 probably due to the special structural geometry of the bis(μ-oxo)-bridged W_1 and W_2 atoms.

As for the β-isomer, all the resonance lines of the γ-dodecatungstosilicate anion are shifted toward high field with respect to the unique line of the α-isomer. Moreover, the barycenters of the respective spectra are along the following sequence (example for the DMF solution): α (−92 ppm), β (−105 ppm), γ (−124 ppm).

Electronic Spectra. The electronic spectra of α-, β-, and γ-12-tungstosilicates as tetrabutylammonium salts in acetonitrile solutions exhibit absorption bands around 260 nm, assigned to O → W charge transfers in the polyanionic structure (Figure 3). A correlation is expected between the global symmetry of the polyanion and the spectrum. Actually, the narrow line (262 nm, $\epsilon = 4.2 \times 10^4$) in the α-isomer spectrum splits into two broad bands (264 nm, $\epsilon = 3 \times 10^4$; 236 nm, $\epsilon = 2.7 \times 10^4$) in the β spectrum and only broader shoulders appear in the γ

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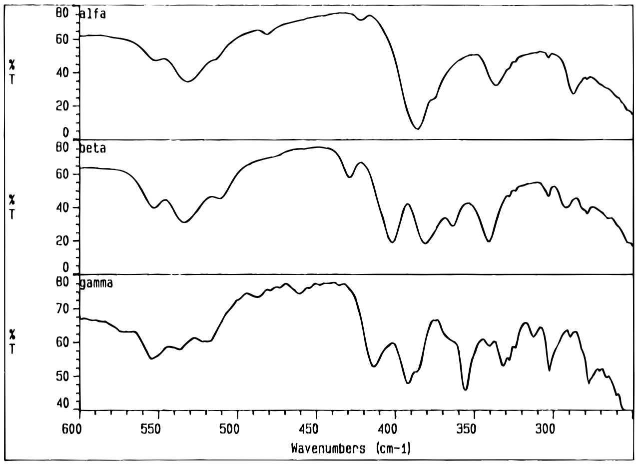

Figure 4. Low-frequency range (below 600 cm^{-1}) of the infrared spectra of the three isomers of $[SiW_{12}O_{40}]^{4-}$.

spectrum, in agreement with decreasing symmetry of the polyanion following the sequence α, β, γ.

Infrared and Raman spectra. It was previously shown[17] that the spectra of tungstic heteropolyanions related to the Keggin structure (α- and β-isomers) can be described by reference to vibrations of the trimetallic group W_3O_{13} and intergroups and the X−O vibrations (X = central atom). It can be expected that decreasing the entire symmetry of the polyanion, $T_d \rightarrow C_{3v} \rightarrow C_{2v}$ in the $\alpha \rightarrow \beta \rightarrow \gamma$ sequence, leads to a splitting of the bands and, then, to a more complex spectrum. This is not really true in the 700−1000 cm^{-1} region, but the changes are more important between γ- and β- than between β- and α-isomers. This is probably related to more important modifications of the intergroup junctions resulting from the bis(μ-oxo) bonds between two tungsten atoms of two different W_3O_{13} groups in the γ structure than in the α and β ones.

The low-frequency region (below 420 cm^{-1} for IR and below 250 cm^{-1} for Raman) is the best spectral region to characterize α- and β-isomers:[18] the number of bands increases from α- to γ-isomer, and the band of lowest frequency shifts along the same sequence: 288, 280, 277 cm^{-1} (Figure 4). The same kind of perturbation is observed in the Raman spectra: the number of lines below 250 cm^{-1} increases, and the lowest frequency shifts (90, 73, 64 cm^{-1}) along the sequence α, β, γ. These changes, once more, can be related to the important modifications of the intergroup junctions.

Stability in Solution. Nonaqueous solutions of the tetrabutylammonium salt of γ-$[SiW_{12}O_{40}]^{4-}$ are very stable. For example, the anion was unchanged after 1 day of boiling of the acetonitrile solution. By contrast, the anion is not stable in pure aqueous solutions, but is stabilized in acidic medium by the addition of organic solvents such as ethanol or dioxane in a 1:1 ratio.

In water, the nature of the compound obtained depends on the pH of the solution. At pH between 4 and 7, the divacant γ-10-tungstosilicate was obtained instantaneously, showing that hydrolytic cleavages occur in the W−O bonds involving the W_1 and W_2 atoms. Then the β- and finally the α-isomer of the 11-tungstosilicate formed slowly by reaction of the γ-10-tungstosilicate with the tungstic species. At pH < 4, in which only α- and β-$[SiW_{12}O_{40}]^{4-}$ anions are stable, only the β-isomer was observed in solution after 1 day.

Addition of equimolar amounts of tungstate to γ-$[HSiW_{10}O_{36}]^{7-}$ at pH = 4−6 (the pH range in which 11-tungstosilicic polyanions can be obtained) leads, within 1/2 h, to a mixture of β_1- and β_2-$[SiW_{11}O_{39}]^{8-}$ (identified by polarography[3]) in nearly equal quantities; the α-isomer is subsequently formed slowly. In the course of the apparition of the β-$[SiW_{11}O_{39}]^{8-}$ anions, a new wave of low intensity appears in the polarogram of the solution and can be tentatively attributed to the existence of the intermediate species γ-$[H_xSiW_{11}O_{39}]^{(8-x)-}$ in small concentrations. In this compound, the additional tungsten atom has three terminal oxygen ligands, and it can be expected that this structural feature should have an unfavorable effect on its stability.

Even though the γ-11-tungstosilicate polyanion cannot be obtained in a pure state, it has been identified as a subunit of a more complicated structure. When tungstate was added to γ-$[HSiW_{10}O_{36}]^{7-}$ in aqueous acidic solution in a molecular ratio of about 1:1, a new tungstosilicic species was isolated. The determination of its structure by single-crystal X-ray diffraction showed that the polyanion is $[H_2Si_2W_{23}O_{78}]^{8-}$ and results from the association of γ-$SiW_{10}O_{36}$ and γ-$SiW_{11}O_{39}$ structural units by a ditungstic group.[19] The occurrence of the γ-11-tungstosilicate polyanion as part of a larger structure is an argument in favor of the proposed mechanism of reaction of tungstate species with the γ-10-tungstosilicate.

Reduced Derivatives. Because of the instability of γ-$[SiW_{12}O_{40}]^{4-}$ in aqueous medium, its electrochemical properties were first investigated in nonaqueous medium. In acetonitrile solution, cyclic voltammetry of the tetrabutylammonium salt of γ-$[SiW_{12}O_{40}]^{4-}$ shows a reversible monoelectronic wave at $E_{1/2} = -0.58$ V/SCE. Under the same conditions, the β- and α-isomers exhibit also a monoelectronic wave at respectively −0.62 and −0.73 V. So, the reducibility of the isomers increases in the series α−β−γ, as the number of rotated trioxotungstic groups.

It is well-known that the reduced species, which have a higher charge, are more stable in aqueous solution than the oxidized parents. As a consequence, the reduced derivatives of the γ-$[SiW_{12}O_{40}]^{4-}$ ion can be prepared in aqueous solution. Because of their characteristic blue color, the formation of the reduced species can be monitored by visible spectroscopy. Direct and quantitative formation of the two-electron-reduced derivative γ-$[SiW^{VI}_{10}W^{V}_{2}O_{40}]^{6-}$ was observed when hydrochloric solution of W^V was added to an aqueous solution of γ-$[HSiW_{10}O_{36}]^{7-}$. The resulting polarogram in acetic buffer (pH = 4.6) exhibits two anodic one-electron waves (−0.08 and −0.33 V/SCE) and two cathodic two-electron waves (−0.75 and −0.98 V/SCE). As expected, the first anodic waves have less negative potentials than those of β- (−0.14, −0.42 V) and α-isomers (−0.24 V, −0.48 V) in the same medium.

The same reduced compound can be obtained when an aqueous solution of γ-$[SiW_{10}O_{36}H]^{7-}$ is reduced by controlled-potential electrolysis involving a two-electron step[9] on a mercury cathodic pool in acetic buffer. As observed for most of the vacant tungstic polyanions,[20] the reduced divacant compound[21] leads to the dodecatungstic parent. This evolution is slow at room temperature (about 1 day for completion) but is very fast if tungstate ions are added to the solution:

$$\gamma\text{-}[HSiW^{VI}_{10}O_{36}]^{7-} \xrightarrow{2e^-,\ 2H^+}$$

$$\gamma\text{-}[H_3SiW^{VI}_{8}W^{V}_{2}O_{36}]^{7-} \xrightarrow[2W^{VI}\text{ (rapid)}]{\text{slow at 20 °C}} \gamma\text{-}[SiW^{VI}_{10}W^{V}_{2}O_{40}]^{6-}$$

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(21) The two-electron-reduced anion γ-$[H_3SiW^{VI}_8W^{V}_2O_{36}]^{7-}$ is given as triprotonated according to the slope of the $E_{1/2}$−pH plots.

Table 1. Characteristics at pH = 4.7 of the Electronic Spectra of the Reduced Derivatives of the Three Isomers[a,b]

isomer	$[SiW_{12}O_{40}]^{5-}$				$[SiW_{12}O_{40}]^{6-}$		
α	510	740	1290		515	635	1030
	(1000)	(1900)	(1400)		(3500)	(4800)	(3100)
β	510	700*	855	1295	490	670	1220
	(500)	(1000)	(1850)	(1200)	(2050)	(3600)	(3450)
γ	640*	745	840*	1580	610	890	1280
	(1300)	(1700)	(1650)	(900)	(4100)	(3600)	(2350)

[a] Water−ethanol for the γ-isomer. [b] The wavelengths of maxima or shoulders (∗) are indicated on the first line and values of the absorptivity on the second line (in parentheses).

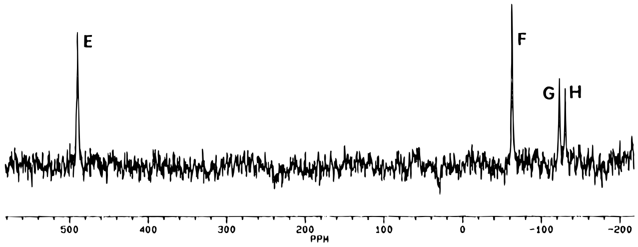

Figure 5. ^{183}W NMR spectrum of the γ-$[SiW_{12}O_{40}]^{6-}$ anion in aqueous solution.

In aqueous acidic solution, the rapid oxidation by permanganate of this compound gives the one-electron-reduced polyanion but disproportionation into the stable two-electron-reduced blue and the unstable oxidized parent occurs:

$$2\gamma\text{-}[SiW^{VI}{}_{11}W^{V}O_{40}]^{5-} \rightarrow \gamma\text{-}[SiW^{VI}{}_{10}W^{V}{}_{2}O_{40}]^{6-} + \gamma\text{-}[SiW^{VI}{}_{12}O_{40}]^{4-}\ \text{(unstable)}$$

In contrast, according to the polarographic behavior, the stable unprotonated one- and two-electron-reduced blues can be obtained by electrolytic reduction of the oxidized anion in a water−ethanol (v/v) mixture. As for the two other isomers, the electronic spectra of the unprotonated reduced compounds exhibit many broad bands. According to previous results,[14] the near-infrared band can be assigned to an intervalence charge transfer between W^V and W^{VI} atoms through μ-oxo bridges, and the other two mainly to d−d transitions. The intervalence charge transfers are significantly lower in energy for the γ−isomer than for the α- and β-isomers (Table 1). In order to understand this difference, it was important to determine whether the structure of the γ-isomer leads to a preferential localization of the electrons on some tungsten atoms of the polyanion. As was shown by Baker et al.,[22] the ^{183}W NMR spectrum of the diamagnetic two-electron-reduced derivative can provide information regarding this question. The ^{183}W NMR spectrum exhibits four resonances denoted E, F, G, and H (from low to high fields) with a 2:2:1:1 intensity ratio, respectively (Figure 5). The observation of this spectrum shows that, as in the Keggin or Dawson structure, the two electrons are spin-paired. Satellites corresponding to W−W coupling are not observed because of the width of the lines. Therefore, it was not possible to assign unambiguously the lines from our results, each line of the reduced species arising from one or the other of the two lines of the same multiplicity in the spectrum of the oxidized species. Line E (+489 ppm, 4W) shows a very large downfield shift as compared to the corresponding lines of the oxidized species [−105 (A) or −128 (C) ppm]. Line F corresponding also to 4W shows a significant downfield shift (−63 ppm vs −105 (A) or −128 (C) ppm]. Lines G and H correspond to 2W and have to be associated with B and D in the spectrum of the oxidized species. Reduction by 2e leads also to a downfield shift of line D assigned to the two bis(μ-oxo) bound W_1−W_2 atoms [−124 (G) or -131 (H) ppm vs −161 (D) ppm]. Only signal B corresponding to the equivalent W_7−W_8 atoms shows a small upfield shift [−124 or −131 vs −117 (B) ppm].

Table 2. Electron Delocalization Parameters Characterizing Each Type of Tungsten Atom in the Diamagnetic 2e-Reduced Derivative Using Two Hypotheses[a]

W_i	$\Delta\delta_i$	x_i	t_i
Wa	+42	0.36	0.18
Wb	−7	0.15	0.07
Wc	+617	1.32	0.66
Wd	+37	0.18	0.09
Wa*	+594	1.28	0.64
Wb*	−7	0.15	0.07
Wc*	+65	0.40	0.20
Wd*	+37	0.18	0.09

[a] In the first hypothesis, line E of the NMR spectrum is assigned to the W_c, and in the second one (∗), line E is assigned to W_a.

According to the model of Baker,[22] this spectrum can be explained by three considerations: (1) The increased shielding resulting from the reduction causes a general upfield shift for all the W atoms (denoted here Δ_1). (2) The change of the chemical shift is downfield (denoted here Δ_2) for each W^V. (3) If the electrons hop on nonequivalent W atoms in the polyoxotungstic structure, this allows one to define a relative residency time, t_i, for each type W_i of tungsten atom. We adopted the value $\Delta_1 = -172$ ppm obtained by Baker with $[P_2W_{18}O_{62}]^{8-}$,[15] which has been successfully used to describe the spectrum of α-$[SiW_{12}O_{40}]^{6-}$.[14] The value of Δ_2 can be estimated using the electronic spectrum of γ-$[SiW_{12}O_{40}]^{6-}$ and the linear correlation between λ and W chemical shift previously demonstrated for Keggin heteropolytungstates.[15] These calculations lead to the value $\Delta_2 = +2380$ ppm for the downfield shift contribution of a W^V. The change in chemical shift observed for each resonance line upon reduction is given[22] by

$$\Delta\delta_i = \Delta_1 + (x_i/(x_i + y_i))\Delta_2$$

where x_i and y_i are respectively the time-average number of W^V and W^{VI} for each type W_i of tungsten atom ($x_i + y_i = 2$ or 4). Unfortunately, we do not know $\Delta\delta_i$ values since we do not have a one-to-one correspondence between the resonance lines of the reduced and the oxidized species. Thus, two different hypotheses can be adopted: line E at +489 ppm which shows a large downfield shift is attributed either to the four equivalent atoms W_c or to the four atoms W_a and conversely for line F. The assignment of the two other lines G and H to W_b or to W_d has no effect on the calculated values of x_i, since they appear at about the same frequency (−124 or −132 ppm). The x_i values and the fractions of time $t_i = x_i/\sum x_i$ which the hopping electron spends on W_i atoms are reported in the Table 2. The value $\sum x_i = 2.01$ is obtained whatever the hypothesis [i.e., as expected because of the large value of Δ_2 (2380 ppm) compared to the difference of the chemical shifts of W_a and W_c in the oxidized species (23 ppm)]. Indeed, the values of the relative residence times calculated from the simple model of Baker are only approximate values, but they indicate a major contribution of one group of four W atoms for the hopping of electrons ($t_c = 0.66$ or $t_a = 0.64$ depending on the assignment). In fact, the W_c atoms are directly linked by μ-oxo junctions, but the four other equivalent W_a atoms are separated by the W_b and W_d atoms in two groups of 2W. Since it has been shown that the added paired electrons prefer to reside on metallic atoms which are relatively close to one another,[22] it can be expected that the

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electrons are preferentially localized on the four W_c atoms opposite the two bis(μ-oxo)-bound tungsten atoms.

Conclusion

The presence of a bis(μ-oxo) junction between two tungsten atoms in the γ-dodecatungstosilicate anion arising from the rotation of two trioxotungstic groups in the α Keggin structure results in no decrease in the stability of the polyanion in organic solvents but results in a sensitivity to hydrolysis in aqueous solution. When two electrons are introduced into the structure, they are delocalized on the NMR time scale on all the tungsten atoms by electron hopping. The variations of bond distances and angles of the oxo junctions between the tungsten atoms lead nevertheless to a preferential residence on four of the twelve tungsten atoms.

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