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Vibrational Investigations of Polyoxometalates. 3. Isomerism in Molybdenum(VI) and Tungsten(VI) Compounds Related to the Keggin Structure

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The comparison between the vibrational (IR and Raman) spectra of a number of α- and β-$XM_{12}O_{40}^{n-}$ polyoxoanions (X = Si^{IV}, Ge^{IV}, P^{V}, As^{V}; M = Mo^{VI}, W^{VI}; all with the tetrabutylammonium counterion) has been performed. The differences between the spectra of the isomers are discussed in terms of trimetallic "ligand" vibrations and "interligand" vibrations. A good correlation between structural and vibrational data is observed for all the tungstic and molybdic α isomers and for the tungstic β isomers. The different behavior of the tungstic and molybdic β isomers is discussed in relation with the possible structures and the greater capability of the molybdenum framework to undergo a rearrangement when subjected to a perturbation.

Introduction

In part 2 of this series,[1] we studied the cation-size effect on the vibrational spectra of α- and β-$XM_{12}O_{40}^{n-}$ polyoxoanions (X = B^{III}, Si^{IV}, Ge^{IV}, P^{V}, As^{V}; M = Mo^{VI}, W^{VI}; abbreviated α- and β-XM_{12}). We concluded that electrostatic interactions are responsible for increases in metal–oxygen stretching frequencies. These interactions can be neglected when the counterion is large enough to force the anions to stay far apart (as is the case for the tetraalkylammonium $(C_nH_{2n+1})_4N^+$ cations, $n \geq 4$); hence the tetrabutylammonium (TBA) compounds can be used as models for isolated anions in the crystal lattice.

As another result of this previous study, we showed that vibrational spectroscopy is able to detect tiny effects acting on these bulky polyoxo complexes. Hence, since just a little is known about the structure of the so-called β-XM_{12} isomers, we report here a vibrational comparison of a number of α- and β-XM_{12} compounds, with the hope that vibrational spectroscopy will give information about the actual structure of some of them.

Experimental Section

The sample preparations and the experimental conditions for obtaining the IR and Raman spectra of the solid compounds were described elsewhere.[1] For the Raman spectra of solutions, classical static techniques (0.3-mL parallelepipedic glass cell) were used for most tungstic compounds and rotating-sample techniques (special liquid cell rotated at about 1000 rpm) for the yellow molybdic compounds in order to prevent the decomposition and/or the reduction by the laser beam. Polarization studies were carried out on dimethylformamide (DMF) solutions.

Abbreviations used: TMA = $[(CH_3)_4N]^+$; TBA = $[(n\text{-}C_4H_9)_4N]^+$; α- (or β-) XM_{12} = α- (or β-) $XM_{12}O_{40}^{n-}$; α- (or β-) XM_{12}TBA = α- (or β-) $TBA_nXM_{12}O_{40}$.

Isomerism of XM_{12} Polyoxoanions

Before starting the comparison of the IR and Raman spectra of these isomers, it is important to briefly report the earlier studies about them.

The existence of isomers is known from the early works on the heteropolyanions (HPAs).[2] However, the knowledge about the isomerism of molybdic and tungstic 12-HPAs (XM_{12}) was only developed during the last two decades, after the works of Souchay and his team (referred to as the "Parisian school").[3] The α–β nomenclature, first introduced by Strickland[4] for the $SiMo_{12}$ isomers, was extended by the Parisian school to all the pairs of isomers reported until now (namely SiW_{12} and GeW_{12} and $SiMo_{12}$, $GeMo_{12}$, PMo_{12}, and $AsMo_{12}$) on the following bases:

Table I. Structural Information about $XW^{VI}{}_{12}$ and $XMo^{VI}{}_{12}$ Anions

			metal NMR[a]	
anion	type of isomer	structure	no. of lines (rel intens)	ref
SiW_{12}	α	K_0	1	9
SiW_{12}	β	K_1	3 (1/2/1)	10
GeW_{12}	α	?	1	9, 11
GeW_{12}	β	?	3 (1/2/1)	11
PW_{12}	only one isomer[5]	K_0	1	9
AsW_{12}	only one isomer	?	1	11
H_2W_{12}	metatungstate (α?)[13]	?	1	9, 10
H_2W_{12}	tungstate X (β?)	?	3 (1/2/1)	10
BW_{12}	quadratic (α?)[13]	?	1	9
BW_{12}	hexagonal[13]	?	>12	13
$SiMo_{12}$	α	K_0		
$SiMo_{12}$	β	?		
$GeMo_{12}$	α	K_0		
$GeMo_{12}$	β	?		
PMo_{12}	α	K_0		
PMo_{12}	β	?		
$AsMo_{12}$	α	?		
$AsMo_{12}$	β	?		

[a] For ^{95}Mo NMR, see ref 12.

(i) The β isomers are more reducible than the α ones: the polarograms of the α and β isomers are similar except for the half-wave potentials (the first reduction waves of the β isomers up to the 4e species are shifted toward positive potentials (see polarographic characterizations in ref 1).

(ii) The absorption spectra in the visible spectral region are similar, except for the molar absorption coefficients, which are higher for the β isomers than for the α ones.

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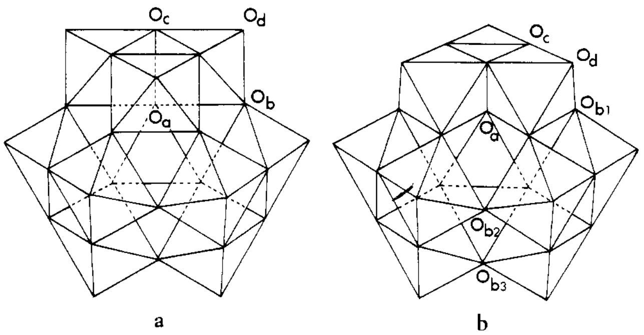

Figure 1. Coordination polyhedra as a representation of (a) the K_0 structure (Keggin structure) and (b) the K_1 structure (β-SiW_{12} structure).

(iii) The isomerization always occurs in the direction $\beta \rightarrow \alpha$ for the nonreduced species (it happens in the opposite direction for the molybdenum 4e-reduced species). The isomerization rate is greater in aqueous solutions for the molybdic compounds than for the tungstic ones: it can be slowed down by using hydro-organic or nonaqueous media. In this manner β isomers of molybdic HPAs were able to be prepared.[1]

The crystalline structures of a number of XM_{12} compounds have been determined. Two types of structures have been reported.[5] The former is the well-known Keggin structure (Figure 1a), named K_0 in the following, established first on PW_{12} and then on α-SiW_{12}, α-PMo_{12}, α-$SiMo_{12}$, and α-$GeMo_{12}$.[6] The latter, named K_1, has been determined on only one anion, namely β-SiW_{12} (Figure 1b).[7,8]

Structural information obtained from crystallographic determinations and from the recently developed metal NMR studies on XM_{12} HPAs is summarized in Table I. From the observations of Table I, and from the polarographic data,[1] we can make some correlations leading to the following considerations and suggestions:

(i) The α nomenclature can be extended to any anion exhibiting the K_0 structure: thus PW_{12} is called α-PW_{12}.

(ii) There is a close relation between the polarograms of XM_{12} and $X'M_{12}$ parent anions (X and X′ having the same oxidation state, as Si^{IV} and Ge^{IV} or P^{V} and As^{V}): this can be considered as a sign of structural identity and will be used so below.

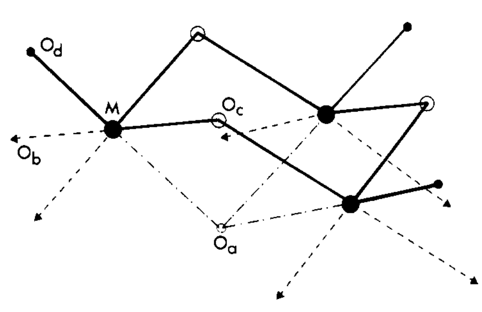

Figure 2. The trimetallic M_3O_6 ligand.

(iii) The existence of a single ^{183}W NMR signal is consistent with one type of W atom: it is a required but not sufficient condition for assuming the K_0 structure. This fact, coupled with a close electrochemical relation with a parent HPA that presents the K_0 structure, allows us to assume that α-GeW_{12} (compared to α-SiW_{12}) and AsW_{12} (compared to α-PW_{12}) have the K_0 structure (hence AsW_{12} is called α-AsW_{12}). In the absence of supplementary electrochemical criteria, some doubt stands about the structure of BW_{12} and H_2W_{12}.[13]

(iv) ^{95}Mo NMR cannot give at the moment similar structural information:[12] the close relation between the polarograms of α-$AsMo_{12}$ and α-PMo_{12} (K_0 structure) is the only criterion for assuming that α-$AsMo_{12}$ has the K_0 structure as well.

(v) From the ^{183}W NMR studies, β-GeW_{12} involves three structurally different types of W atoms, which is consistent with the K_1 structure. As above, the electrochemical similarity with β-SiW_{12} (K_1 structure) makes the assumption of K_1 structure quite likely. The structural homogeneity of the β-tungstic family, which unfortunately includes only two members, seems then well established.

(vi) Nothing is known about the structure of the β-molybdic isomers, neither from crystallographic determinations nor from ^{95}Mo NMR. As there are five possible structures including four trimetallic groups around an XO_4 tetrahedron[14] (the Keggin structure K_0, the structure K_1 with one rotated group, and the speculative structures with respectively two, three, and four rotated groups, which could be named K_2, K_3, and K_4), the β-molybdic isomers could present one of these structures, except K_0.

The X-ray diffraction methods could solve the problem of the actual structure of the β-molybdic isomers. However, these methods can just give a static view of the framework: they cannot give any information about the dynamic behavior of the α and β isomers. Many physical properties such as redox potentials, thermodynamic stability, electron hopping ability, etc., which have currently been studied on these compounds

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(5) A third structure, called γ-PW_{12} by Fuchs et al. (Fuchs, J.; Thiele, A.; Palm, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 789; *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1418), has been also reported. This kind of structure is also called "pseudo-Keggin" by Sergienko et al. (Sergienko, V. S.; Porai-Koshits, M. A.; Yurchenko, E. N. *Zh. Strukt. Khim.* **1980**, *21*, 111), who studied mixed $PMo_{12-x}V_xO_{40}{}^{(3+x)-}$ anions. However, there is no definite proof of the validity of this structure, since it can be proved that the statistical orientation of the anions in the cell could lead to incorrect structural determinations.

(6) See references cited in ref 1.

(7) Matsumoto, K.; Kobayashi, A.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3146.

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(9) Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1982**, *104*, 5384.

(10) Lefebvre, J.; Chauveau, F.; Doppelt, P.; Brevard, C. *J. Am. Chem. Soc.* **1981**, *103*, 4589.

(11) R. Thouvenot has reported the following ^{183}W NMR results on α-GeW_{12}, β-GeW_{12}, and α-AsW_{12}: (i) α-GeW_{12} (acid in D_2O) exhibits one peak at −79.8 ppm. (ii) β-GeW_{12} (acid in D_2O) exhibits (in addition to a small peak at −79.8 ppm due to the α form) three fundamental peaks with $^{2}J_{W-W}$ satellites at −89.5, −91.6, and −104.0 ppm (intensity ratio 1/2/1). Coupling constants are $^{2}J_{W-W}(\text{intra}) = 8.31 \pm 0.2$ Hz and $^{2}J_{W-W}(\text{extra}) = 20.3 \pm 0.2$ Hz. These results can be compared with the corresponding values for β-SiW_{12} (acid in D_2O): −109.1, −114.0, −129.2 ppm; $^{2}J_{W-W}(\text{intra}) = 8.3 \pm 0.2$ Hz; $^{2}J_{W-W}(\text{extra}) = 20.5 \pm 0.2$ Hz. (iii) α-AsW_{12} (TBA salt in 90/10 (v/v) DMF/acetone-d_6) exhibits one peak at −64.6 ppm.

(12) R. Thouvenot, in preliminary NMR measurements on ^{95}Mo at 16.3 MHz (magnetic field 5.9 T) revealed that the line width ($\Delta\nu_{1/2}$) exceeds a few hundred Hz (more than 20 ppm) in most molybdenum-containing polyoxoanions, which is not promising for discriminating the isomers. We plan to carry out the NMR studies in such conditions where the broadenings of the peaks are minimized and/or with a higher field NMR spectrometer.

(13) Although structural determinations on compounds related to the "true" metatungstate $H_2W_{12}O_{40}{}^{6-}$ (noted H_2W_{12}) have been reported (Reduced metatungstate $Rb_4H_8(H_2W_{12}O_{40})\cdot 18H_2O$: Jeannin, Y.; Launay, J. P.; Seid Sedjadi, M. A. *Inorg. Chem.* **1980**, *19*, 2933. "three-proton" metatungstate $[(C_4H_9)_3NH]_5H_3W_{12}O_{40}$: Fuchs, J.; Flindt, E. P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 412), they do not bring definite proof of the actual structure of H_2W_{12} (usually assumed to present the Keggin structure). As far as the $BW_{12}O_{40}{}^{5-}$ anions are concerned, two isomers are known (Hervé, G.; Tézé, A. *C. R. Seances Acad. Sci., Ser. C* **1974**, *278*, 1417): the former, the so-called quadratic $BW_{12}O_{40}{}^{5-}$ (noted BW_{12}), is usually considered as pertaining to the Keggin structure (without structural determination); the latter, often called $BW_{12}(h)$ (as hexagonal) could likely not be an authentic isomer of the former: it might be more condensed, as suggested by ^{183}W NMR studies (Thouvenot, R., unpublished results). The "true" metatungstate H_2W_{12} and the dodecatungstoborate BW_{12} have the same polarographic behavior, which is different from that of the other XW_{12} anions. This experimental fact, combined with the lack of information about the structure of both compounds, allows us to rule them out of our discussion, at least at the moment.

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Table II. Some Assignments Corresponding to the M_3O_6 Ligand Vibrations and to the Interligand Vibrations of Solid α- and β-XM_{12}TBA[a]

	trimetallic ligand vibrations					interligand vibrations			
	ν_s-($M-O_d$) R*	ν_{as}-($M-O_d$) R**	ν_{as}-($M-O_d$) IR	ν_s-($M-O_c-M$) R*	ν_{as}-($M-O_c-M$) IR	ν-($M-O_b-M$) R**	ν-($M-O_b-M$) IR	"ν-($M-O_a$)" R*	ν_{as}-($X-O_a$) IR
α-SiW_{12}	987	966	967	560	797	924 906 886	883	218.5	920
β-SiW_{12}	988.5	968.5	969	554	809 793	909 891 878	870	210	914
α-GeW_{12}	986	964	965	567	780	895	895 885	221	830
β-GeW_{12}	986.5	964.5	967	543	780	906 895 864	890 875	212	830
α-PW_{12}	1003.5	993	987 976	533	810	925 918.5 898	895	215.5	1080
α-AsW_{12}	1000.5	984	983	525	793	919 905 877	873	220.5	912
α-$SiMo_{12}$	967.5	941.5	945 940	620.5	795	883.5	868	246.5	899
β-$SiMo_{12}$	970.5	943.5	945	628	800	895 874	857	245	895
α-$GeMo_{12}$	967.5	940	939	621	778	875	873	247	812
β-$GeMo_{12}$	970	942	945	628	773	907	875	246	812
α-PMo_{12}	986	964	965 955	603	805	894	880	246	1063
β-PMo_{12}	988	968	965 953	605	804	885	882	244	1056
α-$AsMo_{12}$	986	961	965	602	790	880	855	247	895
β-$AsMo_{12}$	987	965	965	608	788	893 862 821	?	244.5	890

[a] These assignments are only an approximation, since all the modes, except the $\nu(M-O_d)$ modes, are more or less mixed, as explained in the text. Abbreviations: R = Raman (*, polarized in DMF solution; **, depolarized in DMF solution); IR = infrared. Frequencies are in cm^{-1}.

for catalytic or other technical applications, cannot be discussed on the basis of crystallographic data alone. Moreover, as pointed out in ref 5, the possibility of statistical orientation of the anions in the cell can lead to ambiguous results.

Vibrational spectroscopy techniques are capable of giving useful information about the structure and the dynamics of a system. Moreover, when used with sufficient and methodic care, they are able to detect tiny differences, as pointed out in the Introduction. Only a little is known about the general vibrational behavior of α- and β-XM_{12} compounds. The published papers are restricted to a few compounds: the dodecatungstosilicates and -germanates as K salts,[15] the dodecamolybdosilicates as TBA salts,[16] α-dodecatungstosilicate as a TMA salt, β-dodecatungstosilicate as a TBA salt,[8] and the dodecamolybdosilicic acids.[17] However, it is obvious that Tarasova et al.[17] did not get the true β isomers. Moreover Fuchs et al.[8] did not pay attention to the cation effect. We have recently shown that the comparisons are only significant when realized with the same counterion, especially on XM_{12} as TBA salts, considered as the best models for isolated anions.[1]

Hence the vibrational study deals with the following compounds: α- and β-SiW_{12}, α- and β-GeW_{12}, α-PW_{12}, α-AsW_{12}, α- and β-$SiMo_{12}$, α- and β-$GeMo_{12}$, α- and β-PMo_{12}, and α- and β-$AsMo_{12}$, all as TBA salts (the dodecatungstoborates and the metatungstate have been ruled out of our discussion, as explained in ref 13). We assume, as a starting point, that all the β isomers present the K_1 structure (which is only proved for the two tungstic isomers), and we shall discuss the validity of this assumption, the differences in behavior of the tungstic and molybdic compounds, and the characterization criteria that can be pointed out from the vibrational data.

Structural Descriptions

The K_0 structure is made up of one XO_4 tetrahedron surrounded by four trimetallic groups of three edge-sharing MO_6 octahedra. The trimetallic groups are linked together by sharing oxygen atoms named O_b (Figure 1a) (T_d symmetry). The K_1 structure is derived formally from K_0 by rotating one of the four trimetallic groups by 60° about its threefold axis (Figure 1b) (C_{3v} symmetry).

The common features of both structures are the central tetrahedron and the four trimetallic groups. We could then alternatively describe the anions as the association of one XO_4 tetrahedron and four trimetallic "ligands" M_3O_6 (Figure 2), those ligands being linked together through 12 μ-oxo junctions achieved through the twelve O_b atoms. The differentiation between the isomers arises from the kinds of interligand junctions.

For the K_0 structure, all the 12 interligand junctions are of the same type, called "2–2" junctions, as shown in Figure 3a. For the K_1 structure, six of the interligand junctions are as above ("2–2" junctions), and the other six are "1–2" junctions, as shown in Figure 3b.

Results and Discussion

(i) General Considerations. The IR and Raman spectra of tungstic and molybdic compounds are shown in Figures 4–9. Some frequencies of relevance in the discussion are presented in Table II with their assignments.

When the polyanion is considered as a whole, the symmetries of the α and β isomers are respectively T_d and C_{3v}. Then the

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(16) Thouvenot, R. Thèse Doctorat ès Sciences Physiques, University of Paris, 1978.

(17) Tarasova, N. S.; Kazanskij, L. P.; Dorokhova, E. N. *Zh. Neorg. Khim.* **1981**, *26*, 625.

Table III. W-O_b-W Angles in the K_0 and the K_1 Structures

anion	cation	W-O_b-W,[a] deg	R[d]	ref	anion	cation	W-O_{b_1}-W,[b] deg	W-O_{b_2}-W,[c] deg	W-O_{b_3}-W,[c] deg	R[d]	ref
α-SiW_{12}	K	151	0.102	6	β-SiW_{12}	K	145	158	142	0.138	7
α-SiW_{12}	Ba	151	0.13	6	β-SiW_{12}	TBA	139	156	144	0.106	8
α-SiW_{12}	TMA	153	0.057	8							

[a] Mean of the 12 values (the 12 O_bs are symmetrically equivalent in the idealized T_d symmetry). [b] Mean of the six values (the six O_{b_1}s are symmetrically equivalent in the idealized C_{3v} symmetry). [c] Mean of the three values (the three O_{b_2}s and the three O_{b_3}s are respectively symmetrically equivalent in the idealized C_{3v} symmetry) (for the explanation of the symbolism, see Figure 1). [d] R = reliability factor.

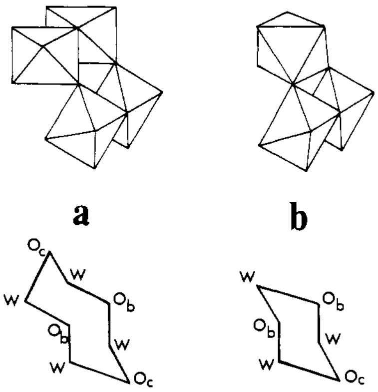

Figure 3. Interligand junctions: (a) "2–2" junctions (in both K_0 and K_1 structures); (b) "1–2" junctions (only in the K_1 structure).

vibrational spectra of the β isomers are expected to be more complex than those of the α isomers (each F_2 mode of the T_d group gives rise to two (A_1 + E) modes in the C_{3v} group, and some symmetry-forbidden modes become allowed). These splittings are not observed in the spectra of the β isomers. This means that this classical approach is not well adapted to the study of such compounds. Thereby we have thrown it out, and we have tried another way to explain the differences between the spectra.[18]

Another approach can be made, which considers the M_3O_6 ligands linked through the O_b atoms. If the concept of group frequencies holds for these M_3O_6 groups, which remain quite similar in both structures and then must lead to similar frequencies, the spectra of the different isomers should differ only in the spectral regions characteristic of the "interligand" vibrations.

This approach can be attempted because the vibrational spectra of a number of polyoxo complexes of different structures having in common these trimetallic groups present the same features, which can be assigned and proposed as approximate "group frequencies" of the M_3O_6 group.[16] The following assignments can be made: $\nu_s(M-O_d)$, as a strong polarized Raman band (1000–960 cm^{-1}), $\nu_{as}(M-O_d)$, as a medium or weak Raman band and a strong IR band (1000–950 cm^{-1}), $\nu_{as}(M-O_c-M)$, as a strong IR band (at about 800–750 cm^{-1}), and $\nu_s(M-O_c-M)$, as a weak or medium polarized Raman band (650–500 cm^{-1}).

(ii) Tungstic Compounds. First, the "characteristic group frequencies" of the tritungstic ligand W_3O_6 can be recognized in all the compounds. As shown in Table II, there are only minor modifications of the W_3O_6 unit vibrations. This result agrees with the structural determinations[7,8] showing that the geometry of the rotated tritungstic unit is similar to that of the nonrotated units. This is consistent with a relative rigidity of the tungstic framework, as already suggested.[16,19]

Secondly, the "interligand" vibrations have to be considered. Since the junctions between the ligands are achieved through the 12 O_b atoms, the W–O_b–W vibrations are essentially concerned.

The $\nu_{as}(W-O_b-W)$ stretchings appear as a weak Raman band (or a set of weak Raman bands) and as an IR band, both in the 920–850-cm^{-1} region (see Table II and Figures 4, 6, and 7). The description of these modes as $\nu_{as}(W-O_b-W)$ is only an approximation, because of the cluster character of the framework and of the possibility of mixing with other stretching modes. The IR band is relatively strong for the Ge compounds and considerably less intense for the Si compounds, especially for the β isomers: it is very weak for the β-SiW_{12} TBA salt and is not even observed for β-$SiW_{12}H$.[15] In the case of the Si compounds, we have shown[1] that the $\nu_{as}(Si-O_a)$ vibration, which occurs in the same spectral region, is deeply mixed with the $\nu_{as}(W-O_b-W)$ stretching and thereby presents an important W–O_b–W stretching character. This mixing could be different in both isomers.

If these observations are taken into account, the α–β comparison can be made: in this spectral region, small but significant modifications are observed between the spectra. These changes can be related to the different kinds of junctions between the tritungstic units through the O_b atoms (Figure 3). This can lead to different W–O_b–W stretching frequencies through the modifications of the W–O_b–W angles (see Table III), which are some of the parameters acting on the frequency values, and the stronger coupling in the case of six-membered rings (two W–O_b–W oscillators with one common W atom).

The spectral changes are much more important in the low-frequency region (below 400 cm^{-1}), which is the best spectral region to characterize both isomers. It is rather difficult to propose assignments in this region characteristic of complex motions involving the bending of various angles and the stretching of W–O_a bonds, which cannot happen without bridge stretching. Thus the Raman polarized band roughly assigned as "$\nu_s(W-O_a)$" (the breathing of the whole polyoxoanion framework around the XO_4 tetrahedron) likely presents an important bridge-stretching character: indeed, this band can be closely related to the so-called "$\nu_s(Mo-O_{central})$" mode for the hexamolybdate anion, a band which, from a normal-coordinate analysis, was proved to be essentially assigned as $\nu(Mo-O_{bridge}-Mo)$.[20] This "$\nu_s(W-O_a)$" band is observed at about 220 cm^{-1} for the α isomers and at about 210 cm^{-1} for the β isomers. Because of the complex character of this mode, it is not obvious to interpret the lowering of its frequency for the β isomers. The relative important shift is then likely related to the modifications of junctions between the tritungstic units, leading, in particular, to a spread of the W–O_b–W angle values, as seen in Table III.

For the other low-frequency Raman-active bands, in the absence of precise assignments, we can just point out the

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[18] Note that the splitting of the $\nu_{as}(W-O_d)$ band (Raman active) observed by Fuchs et al.[8] on α-SiW_{12}TMA and considered as a characteristic of the α isomer disappears in DMF solution: it is certainly due to a crystal effect that can be observed with both isomers as TBA salts. Moreover, the 945-cm^{-1} band observed in the IR spectrum of α-SiW_{12}TMA is not characteristic of the anion, as suggested by Fuchs, since it is not observed with other cations.

[19] Rocchiccioli-Deltcheff, C.; Thouvenot, R. *J. Chem. Res., Synop.* **1977**, 46; *J. Chem. Res., Miniprint* **1977**, 549.

[20] Rocchiccioli-Deltcheff, C.; Thouvenot, R.; Fouassier, M. *Inorg. Chem.* **1982**, *21*, 30.

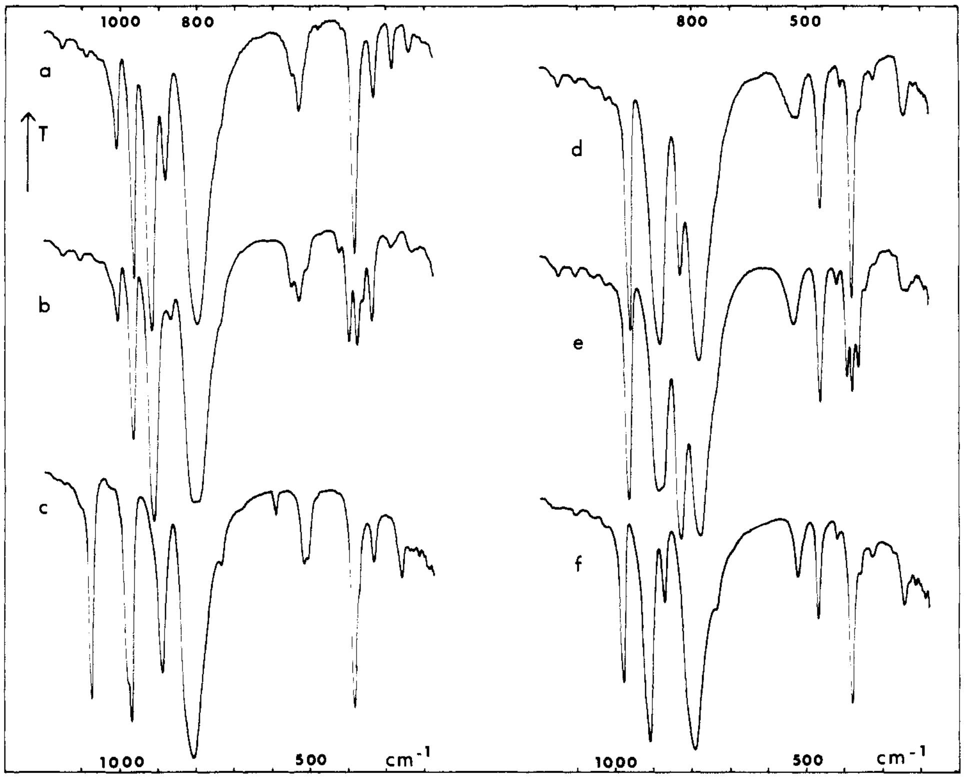

Figure 4. IR spectra of tungstic α and β isomers (as RbI pellets): (a) α-SiW$_{12}$TBA; (b) β-SiW$_{12}$TBA; (c) α-PW$_{12}$TBA; (d) α-GeW$_{12}$TBA; (e) β-GeW$_{12}$TBA; (f) α-AsW$_{12}$TBA.

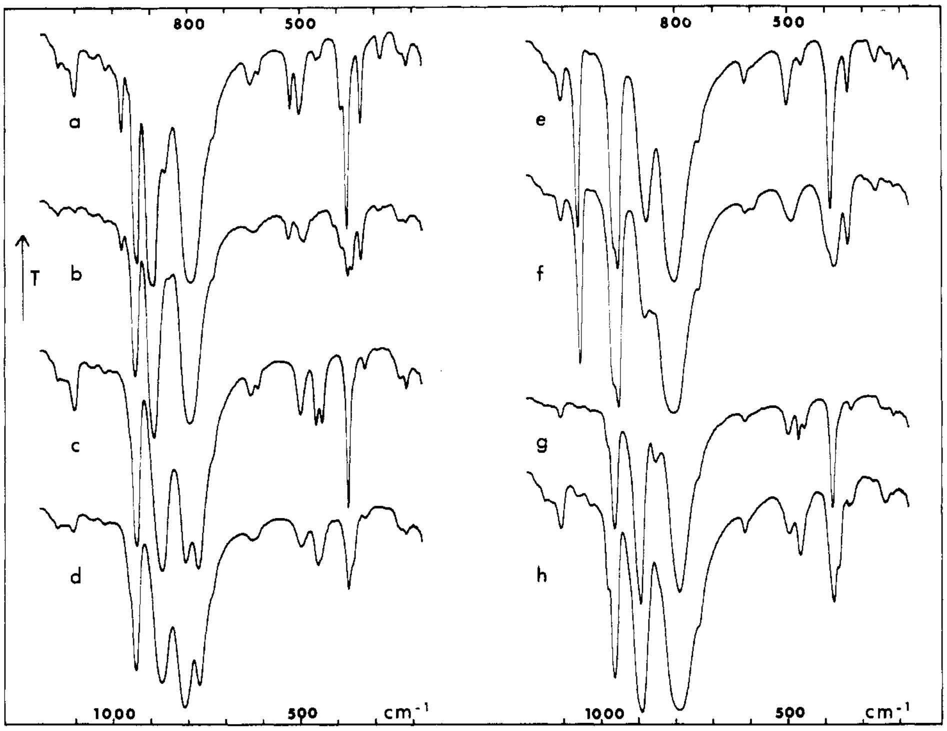

Figure 5. IR spectra of molybdic α and β isomers (as RbI pellets): (a) α-SiMo$_{12}$TBA; (b) β-SiMo$_{12}$TBA; (c) α-GeMo$_{12}$TBA; (d) β-GeMo$_{12}$TBA; (e) α-PMo$_{12}$TBA; (f) β-PMo$_{12}$TBA; (g) α-AsMo$_{12}$TBA; (h) β-AsMo$_{12}$TBA.

differences that can be used for the identification of the isomers. The β-SiW$_{12}$ and β-GeW$_{12}$ anions can be characterized by two bands at 138–140 cm^{-1} (partially polarized) and 73–74 cm^{-1} (depolarized).

Let us now consider the IR spectra below 400 cm^{-1}, especially in the 400–300-cm^{-1} range. All the spectra of the α isomers exhibit the same pattern of two bands: the former strong and sharp at about 370–380 cm^{-1} and the latter medium or weak at about 340 cm^{-1}. Both bands can be considered as characteristic of the α form. Indeed this spectral region is deeply modified for the β isomers: the two bands above are replaced by a set of several well-defined and sharp bands (see Figure 4). These changes with respect to the α-isomer spectra can again be related to the different types of interligand junctions, the modifications of the W–O$_b$–W angles giving rise to several well-separated bands.

In addition, the ν_{as}(X–O$_a$) IR mode has to be considered. A lowering (920 → 914 cm^{-1}) of the ν_{as}(Si–O$_a$) frequency

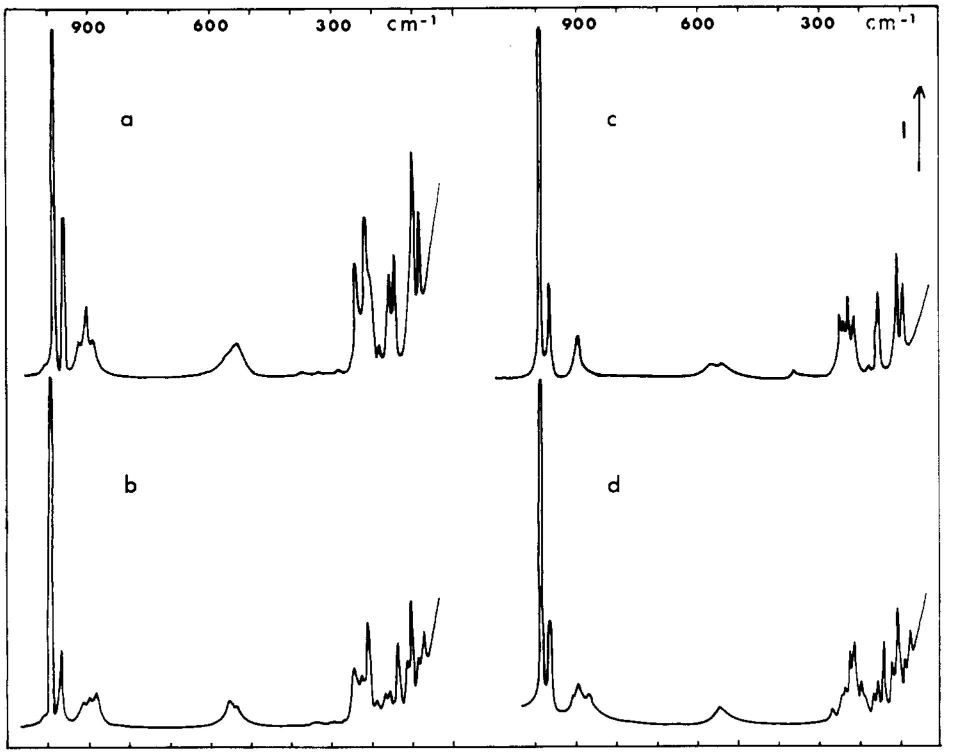

Figure 6. Raman spectra of tungstic α and β isomers (as powdered samples): (a) α-SiW$_{12}$TBA; (b) β-SiW$_{12}$TBA; (c) α-GeW$_{12}$TBA; (d) β-GeW$_{12}$TBA.

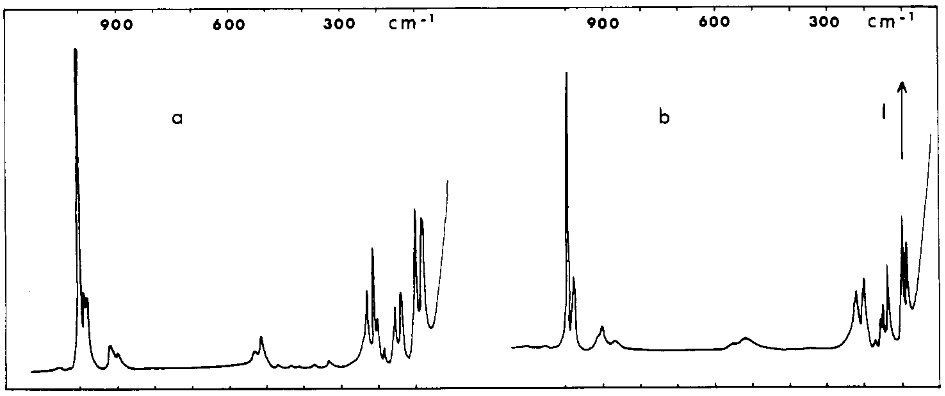

Figure 7. Raman spectra of tungstic α isomers (as powdered samples): (a) α-PW$_{12}$TBA; (b) α-AsW$_{12}$TBA.

could be consistent with a lengthening of the Si–O$_a$ bonds. Such a lengthening is actually observed by Fuchs et al.[8] for β-SiW$_{12}$TBA (mean of the three Si–O$_a$ bond lengths corresponding to the three nonrotated groups, 1.77 Å; Si–O$_a$ bond length corresponding to the rotated group, 1.63 Å; mean of the four Si–O$_a$ bond lengths for α-SiW$_{12}$TMA, 1.64 Å).[21] For β-SiW$_{12}$, the local symmetry of the tetrahedron is lower than T_d; however, no splitting can be observed because of the strong mixing of the ν_{as}(Si–O$_a$) vibration with the W–O$_b$–W stretching. So far as the Ge compounds are concerned, it seems that the GeO$_4$ tetrahedra might be quite similar in both isomers.

(iii) Molybdic Compounds. We have followed the same way as for the tungstic compounds; i.e., we have considered the trimolybdic ligand vibrations and the interligand vibrations involving the O$_b$ atoms.

Let us consider the high-frequency region, which involves both kinds of vibrations (ligand vibrations and interligand vibrations as ν(Mo–O$_b$–Mo)). As one goes from α to β, small but significant changes occur, which are practically of the same order of magnitude for both kinds of vibrations (Table II).

It seems that the group frequency approximation, valuable for the tungstic compounds, does not hold as well for the molybdic ones. This could be related to the reduced rigidity of the molybdic framework with respect to the tungstic one, leading to a "delocalization" over the whole structure of the perturbation induced by the rotation of one trimolybdic group: the whole polyoxoanion could not resist a complete rearrangement.[22] Moreover, we could assume that the reduced rigidity induces a more efficient coupling of the trimolybdic ligands through the O$_b$ atoms: as a consequence, a perturbation affecting the interligand junctions could have a greater influence on the ligands themselves.

Another hypothesis could be put forward, namely a different framework for the molybdic β isomers, which could present one of the structures named K$_2$, K$_3$, or K$_4$. However, at this

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(21) The first structural determination of β-SiW$_{12}$[7] pointed out an important distortion of the SiO$_4$ tetrahedron with an important shortening of one of the four Si–O$_a$ bonds (1.37 Å: however, this discrepancy can be due to the fact that the structure is not well refined (R = 0.138).

(22) A common feature of all Mo(VI) oxo compounds is the equatorial distortion of the MoO$_6$ octahedra. More schematically, in an oxide-like structure description, the Mo^{VI} cation is able to occupy different positions of the octahedral cavity.

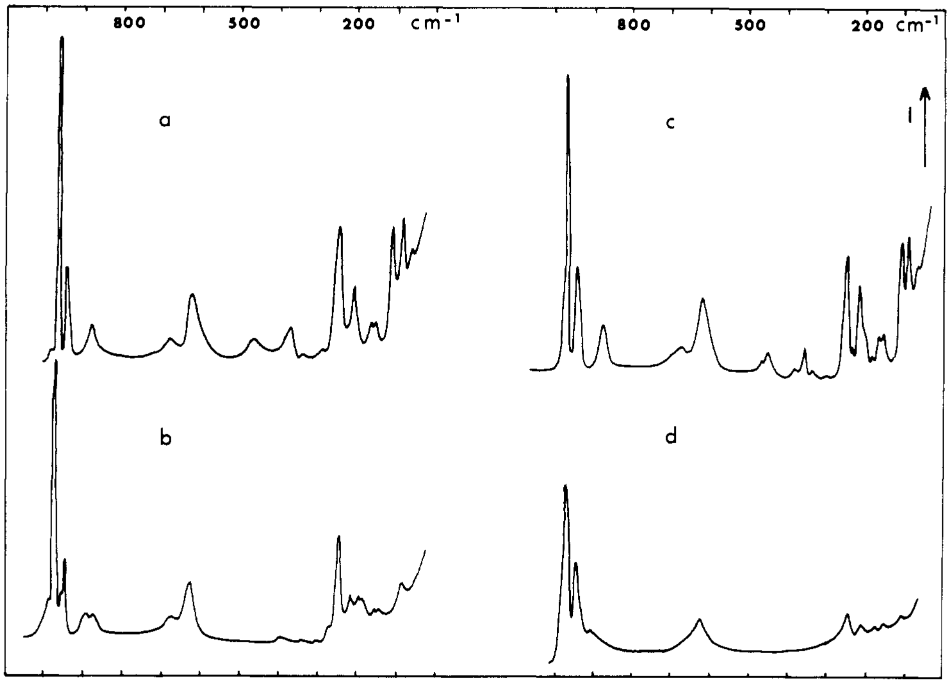

Figure 8. Raman spectra of molybdic α and β isomers (as powdered samples): (a) α-SiMo$_{12}$TBA; (b) β-SiMo$_{12}$TBA; (c) α-GeMo$_{12}$TBA; (d) β-GeMo$_{12}$TBA.

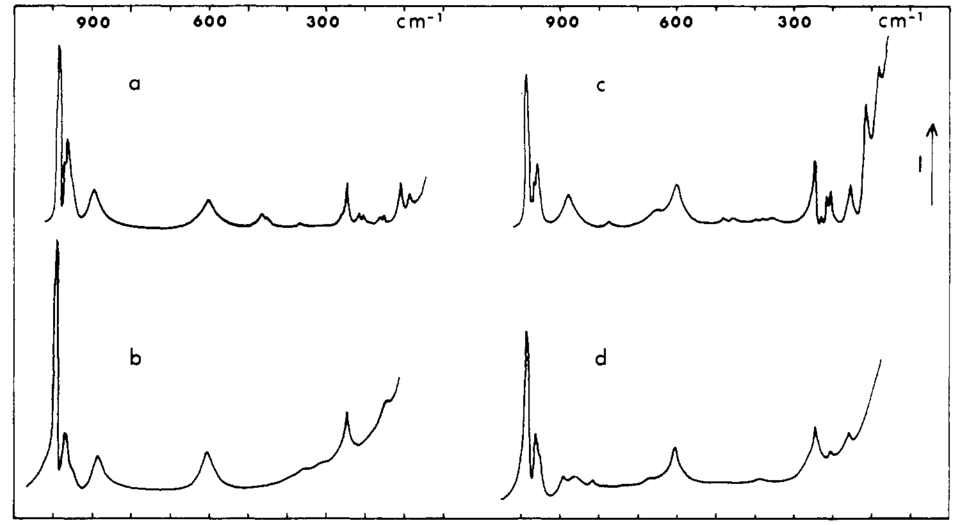

Figure 9. Raman spectra of molybdic α and β isomers (as powdered samples): (a) α-PMo$_{12}$TBA; (b) β-PMo$_{12}$TBA; (c) α-AsMo$_{12}$TBA; (d) β-AsMo$_{12}$TBA.

point, nothing is actually in opposition to the assumption of K$_1$ structure, provided that the supplementary assumption of reduced rigidity is introduced.

Divergences between the behaviors of molybdic and tungstic compounds appear clearly in the low-frequency region (below 400 cm^{-1}), which was pointed out above as the best spectral region to characterize both isomers. The "ν_s(Mo–O$_a$)" Raman polarized band at about 245 cm^{-1} undergoes a very slight lowering for the molybdic compounds (α isomers, ~247 cm^{-1}; β isomers, ~245 cm^{-1}): let us recall that the lowering is much more important for the tungstic compounds (ν_s(W–O$_a$): α isomers = ~220 cm^{-1}; β isomers = ~211 cm^{-1}). This different behavior could be explained by assuming that the greater capability of the molybdic framework for a rearrangement, when it is submitted to a perturbation, induces a less important spread of the Mo–O$_b$–Mo angles and, a fortiori, a smaller change in the frequency values.

The other Raman-active bands observed at lower frequencies cannot help for the comparison between the α and β isomers and between the molybdic and tungstic compounds. Many difficulties arise from different reasons: (1) the assignments are not made; (2) there is a mass effect that makes the correspondencies between the molybdic and tungstic compounds rather uncertain; (3) the bands of the molybdic compounds are relatively less intense than those of the tungstic compounds, which present likely a more important stretching character; (4) the poor quality of the Raman spectra of some molybdic β isomers makes the α–β comparison rather difficult.[23]

In the low-frequency spectral region, we observe in the IR spectra some divergences with respect to those of the corresponding tungstic compounds. In the 400–300-cm^{-1} range, the IR spectra of the molybdic α isomers show, exactly as for the tungstic compounds, the same pattern of two bands (the former sharp and strong at about 370–380 cm^{-1}, the latter, weak or medium, at about 340 cm^{-1}): indeed, these two bands are actually quite characteristic of the α form (tungstic or

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[23] Recall that the Raman spectra of the molybdic β isomers can be only obtained by the rotating-sample technique, because of the high reducibility of the compounds, which are very sensitive to the laser beam.

molybdic). For the β isomers, there is a modification of this spectral region: but, instead of several well-separated and sharp bands, as for the β isomers, only shoulders on broad bands are observed for the molybdic β isomers (see Figure 5). These changes give rise to some ambiguities: either the K_1 structure with a rearrangement of the whole framework due to the reduced rigidity of the molybdic compounds or another structure (K_2, K_3, or K_4) could explain these modifications.

At this point, it is worth noting that all the IR spectra of the α isomers, both tungstic and molybdic, present characteristic common features. As we know that all these isomers have the same structure, namely the K_0 structure, we can make a good correlation between the vibrational spectra and the structure, without requiring any additional assumption about the rigidity of the framework. It is no longer true for the β isomers: indeed, the tungstic isomers have a behavior different from that of the molybdic ones. In the assumption of identical structure for all the β isomers (K_1 structure), we have to introduce a supplementary requirement to explain the divergences between the spectra of molybdic and tungstic compounds. A question may now arise: why is this additional assumption required only in the case of the β isomers, since the reduced rigidity is a peculiarity of the molybdic framework (either α or β)? This argument could be in favor of ruling out the assumption of K_1 structure for the molybdic isomers, unfortunately without a clear-cut proof. The doubts pointed out by the vibrational spectrometry cannot be easily removed.

Last, let us consider the $\nu_{as}(X–O_a)$ band. This is a rather pure vibration only in the case of P compounds. From the IR data, it appears that the T_d local symmetry of the PO_4 tetrahedron is preserved since no splitting is observed for β-PMo_{12}. This is not a proof that the symmetry of the whole polyoxoanion is T_d, since no splitting of the $\nu_{as}(P–O_a)$ band occurs as well for α-$PMo_{11}Ni$, which cannot have this formal symmetry.[19] A significant lowering ($1062 \rightarrow 1056$ cm^{-1}) of the $\nu_{as}(P–O_a)$ frequency is consistent with a lengthening of the $P–O_a$ bonds. Such a lengthening of the $Si–O_a$ and $As–O_a$ bonds could happen for the molybdic β isomers, according to the lowering of the $\nu_{as}(X–O_a)$ frequency (Table II): however, this conclusion has to be considered with some prudence because of the strong mixing with the $\nu_{as}(Mo–O_b–Mo)$ stretching.

Conclusion

From the vibrational investigations of α- and β-XM_{12} isomers related to the Keggin structure, we can point out the following conclusions.

First, the similarity of the vibrational spectra of all the molybdic and tungstic α isomers agrees with their structural identity: all the α isomers likely exhibit the K_0 structure (Keggin structure).

Second, the structural homogeneity of the β isomers does not appear so clearly. Only the two tungstic isomers exhibit similar features consistent with the same structure (K_1 structure). Their vibrational spectra differ from those of the α isomers only in the spectral regions characteristic of the interligand vibrations, the discussion being carried out in terms of tritungstic ligand vibrations and interligand vibrations. The vibrational behavior of the molybdic β anions is complicated with the "reduced rigidity" of the Mo framework with respect to the W one: this peculiarity allows a "delocalization" over the whole structure of the perturbation induced by the rotation of one (or more) trimetallic group. It is then impossible to infer unambiguously the structure of the molybdic β anions from their vibrational spectra. The K_1 structure, still plausible for β-$SiMo_{12}$ and β-$GeMo_{12}$, seems questionable for β-PMo_{12} and β-$AsMo_{12}$. Owing to the different charge distribution, P^V or As^V could destabilize the K_1 structure, not only with respect to K_0 but also with respect to another structure, such as K_2, for example. As suggested by Pope[24] on electrostatic grounds, the K_2, K_3, and K_4 structures are expected to be thermodynamically less favorable than K_0 and K_1. However, in the case of the molybdic compounds, the instability gained from additional electrostatic repulsions could be counterbalanced by the rearrangement of the framework: as a consequence, the K_2 structure, for example, might become thermodynamically more stable than K_1. As this does not hold for the W framework, we could explain the failure to prepare the β isomers of PW_{12} and AsW_{12}, although a lacunary PW_{10} anion related to the K_2 structure was already reported.[25] We are trying to synthesize isomers of PW_{12} and AsW_{12} in order to test these assumptions.

Keeping in mind the above conclusions, it is now interesting to reexamine the vibrational spectra of BW_{12} and of the so-called metatungstate $H_2W_{12}O_{40}{}^{6-}$ (ruled out of our discussion, as explained in ref 13). The (quadratic) BW_{12} anion exhibits some vibrational features of the K_0 structure: it is not so clear for the metatungstate. Investigations about the peculiar features of the metatungstate and of other XM_{12} anions (X = transition metal) are now in progress.

Registry No. SiW_{12}TBA, 51542-99-5; PW_{12}TBA, 53749-37-4; GeW_{12}TBA, 83844-87-5; AsW_{12}TBA, 83844-88-6; $SiMo_{12}$TBA, 59138-97-5; $GeMo_{12}$TBA, 81205-59-6; PMo_{12}TBA, 53749-36-3; $AsMo_{12}$TBA, 81158-05-6.

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