Inorg. Chem. **1983**, *22*, 207-216

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Vibrational Investigations of Polyoxometalates. 2. Evidence for Anion–Anion Interactions in Molybdenum(VI) and Tungsten(VI) Compounds Related to the Keggin Structure

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Received April 2, 1982

A systematic study of the cation-size effect on the vibrational spectra of α- and β-$XM_{12}O_{40}^{n-}$ polyoxoanions has been performed ($X = B^{III}, Si^{IV}, Ge^{IV}, P^{V}, As^{V}$; $M = Mo^{VI}, W^{VI}$). The $M-O_d$ stretching frequencies decrease as the cation size increases. This is attributed to a weakening of anion–anion interactions of the electrostatic type. These interactions vanish for only interanionic oxygen–oxygen distances as long as 6 Å (tetrabutylammonium (TBA) salts). For these polyanions, the approximation for the isolated anion strictly holds with large counterions such as TBA. In addition, some preparations of polyanions are described for the first time.

Introduction

The influence of counterions on the vibrational spectra of complex anions in the solid state has been widely studied by using several kinds of approaches. One of them, based on the factor group approximation, considers the coupling between formula units in the Bravais cell (without regard to the nature of the coupling), which supposes the previous knowledge of the crystal structure of the studied compound. Another more chemical approach considers the anion–cation interactions as perturbations on the charge-density repartition, on the geometry of the anion, and, consequently, on the vibrational spectra, with respect to the isolated anion (in the zero-order approximation often used for the free anion in the gas phase or in solution). This approach does not need the knowledge of the crystal structure and can provide information about the intermolecular interactions. However, the interpretations of the influence of some cations are sometimes contradictory, as, for example, for the alkaline cation effect on tetraoxometalates[1] and on monooxopentafluorometalates or dioxotetrafluorometalates.[2]

Such discrepancies arise from the fact that several effects of the same order of magnitude can act simultaneously: ignoring one of them can provide opposite interpretations. For instance, as alkaline salts of complex anions often crystallize with water molecules, the cation effect should not be dissociated from that of the water molecules, which involve hydrogen bonds.

In order to shed more light on this problem, we present here some results obtained with bulky polyanions of molybdenum and tungsten, related to the Keggin structure. Such polyanions were chosen because they can be obtained with a great variety of counterions, ranging from the strong hydrogen-bond-donor hydroxonium ion $H_5O_2^+$ to the bulky and "inert" tetrahexylammonium cation, through the more or less polarizing alkaline cations. With such a large range of counterions, we expected to differentiate the effects arising from cation size, cation polarizing power, and crystallization solvent molecules.

Experimental Section

(i) Sample Characterizations. The preparations of samples were generally performed in two steps: the synthesis of specific polyoxoanions (coded by roman numerals) and the obtention of various salts (counterions coded by specific letters).

The synthesis of a specific polyoxoanion was performed with an appropriate counterion or in the acidic form. The identification and the isomeric purity were essentially based upon electrochemical properties, especially polarography, which is recognized as a reliable method for such compounds. IR and Raman spectroscopies were also used to check the isomeric purity.

The obtention of the various salts was carried out by neutralization of the acids or by a simple metathesis reaction. In this case, diluted solutions (~0.01 M) were generally required to avoid the precipitation of mixed salts. The efficiency of the purification procedures was followed by thermogravimetry (TG), IR spectroscopy, and Raman spectroscopy. Classical protometric titrations were performed for alkaline and barium salts in order to give the cation content (acidic or neutral salt).

The elemental analysis is not a good criterion for checking the purity of heteropolyoxo compounds, since the mass percentages of some of their constituting elements can be very low (1–2%). Moreover, it is inefficient to differentiate isomers. Thereby, we preferred to choose thermogravimetric analysis (TG), which, coupled with careful spectroscopic and polarographic measurements throughout the sample preparation and purification, allowed us to define unambiguously the compounds.

TG curves generally show two steps. The first one, occurring at temperatures lower than about 120 °C, corresponds to the loss of crystallization water and/or adsorbed water, leading to the anhydrous heteropolyoxo compound, as checked by IR spectroscopy (the term "anhydrous" means no water bands in the IR spectrum). The second step, occurring at temperatures always higher than 200 °C (temperatures varying according to X, M, and the counterion), corresponds to the decomposition of the heteropolyoxo compound, involving the loss of organic material and/or protons (with eventually a volatile oxide such as As_2O_5). For a neutral tetraalkylammonium salt such as $[(n\text{-}C_4H_9)_4N]_4SiM_{12}O_{40}$, noted $(TBA)_4SiM_{12}O_{40}$, the total weight loss, according to the scheme

$$(TBA)_4SiM_{12}O_{40} \rightarrow SiO_2 + 12MO_3$$

corresponds to 64 C + 144 H + 4 N + 2 O, which was expressed under the commodious and concise form 2 "$(TBA)_2O$". For the acids, the *n* protons come off with oxygen, and the cation weight loss was expressed under the form *n*/2 "H_2O" ("constitution" water). In the case of a mixed salt such as $[(n\text{-}C_4H_9)_4N]_4HBW_{12}O_{40}$ the weight loss was expressed as 2 "$(TBA)_2O$" + $^1/_2$ "H_2O" to take into account the departure of the organic material and of the proton. The general term "cation content" will be used below to express for every case these total weight losses in concise form.

IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer as KBr or RbI pellets in the spectral region 1200–200 cm^{-1} and as Nujol or hexachlorobutadiene mulls between NaCl plates in the spectral regions characteristic of water.

Raman spectra were made on a Coderg PH-O spectrometer equipped with a Spectra Physics 164 argon laser (514.5 or 488 nm, 100–500 mW). For most tungsten(VI) compounds, classical static techniques for powder samples were used, i.e., the capillary-tube and the conical-sample techniques. Rotating-sample techniques had to be used for the yellow molybdenum(VI) compounds in order to prevent the decomposition and/or reduction by the laser beam. Powdered samples were pressed in a matrix and rotated at about 1000 rpm.

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(1) Müller, A.; Baran, E. J.; Carter, R. D. *Struct. Bonding (Berlin)* **1976**, *26*, 81.

(2) Dehnicke, K.; Pausewang, G.; Rüdorff, W. *Z. Anorg. Allg. Chem.* **1969**, *366*, 64. Pausewang, G.; Schmitt, R.; Dehnicke, K. *Ibid.* **1974**, *408*, 1.

0020-1669/83/1322-0207$01.50/0

Thermogravimetry was carried out in air on a Cahn RG electrobalance equipped with a Kipp & Zonen Micrograph BD5 recorder coupled with a BA5 channel selector (sample weight 1–10 mg; heating rate 5 °C/min; sensitivity and reproducibility better than 5 μg, i.e., about 1‰ of the sample weight).

Polarographic measurements were performed on a PRG 3 Tacussel polarograph in buffer aqueous or hydroorganic medium with a rotating-carbon (or platinum) electrode for molybdenum compounds and a dropping-mercury electrode for tungsten compounds. All potentials were recorded vs. saturated calomel electrode (vs. SCE).

(ii) Studied Samples. All reagents were analytical grade and were used without further purification. When required, anhydrous solvents were obtained by stirring on 4-Å molecular sieves.

The acidic forms of molybdenum compounds are unstable at room temperature and have to be stored in a refrigerator. All the reported results concern freshly prepared samples. Many compounds are not defined hydrates, a part of the water content being zeolitic. This water content depends on the past of the compound (obtention mode and storage conditions). So the compounds will be noted with x H_2O, except for hydrates unambiguously defined and crystallographically determined. For the whole series, percent TG weight losses were calculated with respect to the anhydrous compound, which seems the most suitable for calculations.

The following abbreviations will be used: Et_2O = diethyl oxide; MeOH = methanol; EtOH = ethanol; Gua = $[C(NH_2)_3]^+$; TMA = $[(CH_3)_4N]^+$; TEA = $[(C_2H_5)_4N]^+$; TPA = $[(n\text{-}C_3H_7)_4N]^+$; TBA = $[(n\text{-}C_4H_9)_4N]^+$; THA = $[(n\text{-}C_6H_{13})_4N]^+$; exptl = experimental; calcd = calculated; vs = very strong; s = strong; m = medium; w = weak; vw = very weak; sh = shoulder.

(A) α-$SiMo_{12}O_{40}^{4-}$ (I) (Noted α-$SiMo_{12}$). (1) α-$H_4SiMo_{12}O_{40}$. (Ia) (Noted α-$SiMo_{12}H$). Ia was prepared according to Fournier's procedure.[3] When the yellow solution (160 mL) was completely transformed into the α form, the acid was extracted by Et_2O (80 mL) after addition of 12 M HCl (40 mL). After separation, the Et_2O layer (80 mL), added with half its volume of water, was put in a vacuum desiccator, over concentrated H_2SO_4, until the formation of yellow octahedral crystals (yield 21 g).

Polarographic characterization: Pt electrode; 0.5 M $HClO_4$ in 1:1 (v/v) water/1,4-dioxane; +0.290 V (2 F); +0.180 V (2 F); –0.060 V (2 F). TG: hygroscopic; water content exptl 15.1%, calcd for 14 H_2O 13.8%; cation content exptl 1.9%, calcd for 2 "H_2O" 1.9%. IR (cm^{-1}): 995 (sh), 957 (s), 904 (vs), 855 (m), 770 (vs), 535 (m), 442 (w), 393 (sh), 370 (sh), 360 (m), 335 (m). Raman (cm^{-1}): 988 (vs), 963.5 (m), 907 (w), 875 (vw), 682 (sh), 632 (m), 451 (vw), 368 (vw), 290 (vw), 250.5 (s), 220 (m), 162 (m), 111 (s), 64 (w).

(2) α-$[C(NH_2)_3]_4SiMo_{12}O_{40}\cdot H_2O$ (Ie) (Noted α-$SiMo_{12}Gua$). Ie was obtained from a metathesis of Ia in about 0.01 M aqueous solution and GuaCl in saturated aqueous solution. Recrystallization was performed in water.

TG: water content exptl 1.1%, calcd for 1 H_2O 0.9%; cation content exptl 13.4%, calcd for 2 "$(Gua)_2O$" 13.2%. IR (cm^{-1}): 990 (w), 980 (w), 957 (sh), 949 (s), 900 (vs), 865 (w), 790 (vs), 615 (w), 530 (sh), 500 (m), 372 (s), 337 (m), 280 (w). Raman (cm^{-1}): 978.5 (vs), 964 (w), 958 (w), 943 (w), 895 (w), 624 (m), 465 (vw), 366 (vw), 249 (s), 213 (m), 163 (m), 118 (s), 63 (w).

(3) α-$[(n\text{-}C_4H_9)_4N]_4SiMo_{12}O_{40}$ (Ik) (Noted α-$SiMo_{12}TBA$). The preparation of Ik was published elsewhere.[3]

TG: anhydrous; cation content exptl 35.8%, calcd for 2 "$(TBA)_2O$" 35.9%. IR (cm^{-1}): 985 (w), 945 (sh), 940 (s), 899 (vs), 868 (sh), 795 (vs), 735 (sh), 635 (w), 600 (sh), 532 (w), 509 (w), 463 (w), 452 (w), 397 (sh), 380 (s), 340 (m), 282 (w). Raman (cm^{-1}): 967.5 (vs), 941.5 (m), 883.5 (w), 686 (w), 620.5 (m), 465 (w), 371 (w), 344 (vw), 290 (vw), 246.5 (s), 208.5 (m), 167 (w), 156 (w), 109.5 (s), 88 (m), 64 (w).

(B) β-$SiMo_{12}O_{40}^{4-}$ (II) (Noted β-$SiMo_{12}$). β-$[(n\text{-}C_4H_9)_4N]_4SiMo_{12}O_{40}$ (IIk) (Noted β-$SiMo_{12}TBA$). IIk was prepared according to a procedure derived from that of Massart[4] for the acid. A 120-mL quantity of a 1 M aqueous solution of Na_2MoO_4 was acidified by 37 mL of aqueous 13 M HNO_3 and added with 200 mL of 1,4-dioxane. Then, 50 mL of a 0.2 M aqueous solution of Na_2SiO_3 was poured dropwise. The solution turned deep yellow and was stored for about 15 h at room temperature. Addition of 20 mL of a (TBA)Br solution (1.9 M in 1,4-dioxane) induced the formation of an oil, which was separated, treated by 1,4-dioxane and Et_2O, yielding 25 g of a crude yellow-orange powder. Recrystallization was performed in anhydrous acetone (10 g/300 mL). After filtration of the less soluble α form (~20% of the crude product), the solution deposited large orange blocks, free of the α form, as checked by polarography.

Polarographic characterization: Pt electrode; 0.5 M $HClO_4$ in 1:1 (v/v) water/1,4-dioxane; +0.390 V (2 F); +0.295 V (2 F); –0.010 V (2 F). TG: anhydrous; cation content exptl 35.7%, calcd for 2 "$(TBA)_2O$" 35.9%. IR (cm^{-1}): 982 (w), 945 (s), 895 (vs), 857 (sh), 800 (vs), 737 (w), 627 (w), 537 (w), 497 (w), 415 (sh), 392 (sh), 377 (m), 365 (m), 340 (m), 288 (w). Raman (cm^{-1}): 970.5 (vs), 953 (sh), 943.5 (m), 895 (w), 874 (w), 677 (w), 628 (m), 399 (vw), 344 (vw), 303 (vw), 273 (vw), 245 (s), 214 (w), 198 (w), 188 (w), 157 (w), 144 (w), 88 (w).

(C) α-$GeMo_{12}O_{40}^{4-}$ (III) (Noted α-$GeMo_{12}$). (1) α-$H_4GeMo_{12}O_{40}\cdot 14H_2O$ (IIIa) (Noted α-$GeMo_{12}H$). Preparation of the germanate stock solution: A 10.5-g quantity of powdered Ge metal (99.999%) was suspended in 60 mL of 6.25 M NaOH in a PTFE beaker. An aqueous H_2O_2 solution (~10 M) was added slowly with stirring until complete metal dissolution (about 50 mL of H_2O_2 in 1 h). In order to achieve the decomposition of the peroxo compounds formed, we stored the solution on a water bath (~80 °C) until no further O_2 evolution. After cooling and filtration, the viscous solution (~50 mL) was diluted to about 400 mL and titrated by protometry ([Ge] = 0.37 M, free $[OH^-]$ = 0.52 M).

Preparation of IIIa: Fournier's procedure[3] was modified as follows: A 40-mL quantity of 13 M HNO_3 was added to 120 mL of a 1 M Na_2MoO_4 aqueous solution. Then 27 mL of the alkaline germanate stock solution was poured in dropwise; the solution turned yellow and was stored at 80 °C for 30 min to effect complete $\beta \rightarrow \alpha$ isomerization. Classical Et_2O extraction (addition of 30 mL of Et_2O) was performed after acidification (addition of 15 mL of 12 M HCl), and the Et_2O layer (25 mL) was treated by using the same procedure as for Ia (yield 20 g).

Polarographic characterization: glassy carbon electrode; 0.5 M $HClO_4$ in 1:1 (v/v) water/1,4-dioxane; +0.330 V (2 F); +0.210 V (2 F); –0.020 V (2 F); –0.175 V (2 F). TG: water content exptl 13.5%, calcd for 14 H_2O 13.9%; cation content exptl 1.9%, calcd for 2 "H_2O" 1.9%. IR (cm^{-1}): 973 (sh), 951 (s), 870 (vs), 790 (vs), 760 (vs), 510 (w), 455 (m), 435 (sh), 362 (s), 323 (m). Raman (cm^{-1}): 986 (vs), 960 (m), 895 (w), 624 (m), 250 (s) (difficult to obtain, even with the rotating-sample technique).

(2) α-$Na_4GeMo_{12}O_{40}\cdot 8H_2O$ (IIIc) (Noted α-$GeMo_{12}Na$). IIIc was obtained by partial neutralization (pH <2) of the saturated aqueous solution of IIIa by 0.1 M aqueous NaOH. Recrystallization was performed in water.

TG: water content exptl 6.9%, calcd for 8 H_2O 6.9%. IR (cm^{-1}): 960 (s), 952 (sh), 945 (sh), 895 (vs), 808 (vs), 775 (vs), 645 (w), 633 (w), 600 (w), 502 (m), 463 (m), 445 (m), 370 (s), 352 (sh), 339 (w), 293 (w). Raman (cm^{-1}): 979.5 (vs), 961.5 (m), 950.5 (m), 943 (sh), 895 (w), 884 (w), 690 (w), 626 (m), 502 (vw), 451 (w), 389 (w), 357 (w), 300 (vw), 255 (sh), 247.5 (s), 229 (w), 218 (m), 187.5 (w), 163 (m), 107 (m), 98 (sh), 93 (s).

(3) α-$[(n\text{-}C_4H_9)_4N]_4GeMo_{12}O_{40}$ (IIIk) (Noted α-$GeMo_{12}TBA$). Preparation of IIIk was published elsewhere.[3]

TG: anhydrous; cation content exptl 35.3%, calcd for 2 "$(TBA)_2O$" 35.3%. IR (cm^{-1}): 960 (sh), 939 (s), 880 (sh), 873 (vs), 812 (vs), 778 (vs), 735 (sh), 635 (w), 605 (sh), 507 (m), 465 (m), 449 (m), 377 (s), 360 (sh), 330 (m), 290 (w). Raman (cm^{-1}): 967.5 (vs), 940 (m), 875 (m), 684 (w), 621 (m), 465 (vw), 456 (w), 388 (vw), 359 (w), 339 (vw), 331 (vw), 247 (s), 232 (vw), 211 (s), 206 (sh), 186 (w), 166 (m), 156 (m), 109 (s), 91 (s), 64 (w).

(D) β-$GeMo_{12}O_{40}^{4-}$ (IV) (Noted β-$GeMo_{12}$). β-$[(n\text{-}C_4H_9)_4N]_4GeMo_{12}O_{40}\cdot xH_2O$ (IVk) (Noted β-$GeMo_{12}TBA$). To 120 mL of a 1 M Na_2MoO_4 aqueous solution was added successively 40 mL of 13 M aqueous HNO_3 and 400 mL of 1,4-dioxane. Then, 27 mL of the germanate stock solution (see part C) was poured in dropwise. The solution turned yellow and was stored for 1 h at room temperature. A solution of 10 g of (TBA)Br in 50 mL of 1,4-dioxane (0.62 M) was then added. The resulting oil was separated and washed by decantation several times with peroxide-free 1,4-dioxane and Et_2O. The resulting powder was air-dried (16 g). Recrystallization was performed in anhydrous acetone. After filtration of the less soluble α form (~8% of the crude product), the solution deposited 11 g of

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(4) Massart, R. Thèse doctorat ès sciences physiques (CNRS AO 1877), University of Paris, 1967; *Ann. Chim. (Paris)* **1968**, *3*, 507.

orange crystals free of the α form, as checked by polarography.

Polarographic characterization: Pt electrode; 0.5 M $HClO_4$ in 1:1 (v/v) water/1,4-dioxane; +0.410 V (2 F); +0.330 V (2 F); –0.040 V (2 F). TG: water content x = 1.2; cation content exptl 35.3%, calcd for 2 "$(TBA)_2O$" 35.3%. IR (cm^{-1}): 970 (sh), 960 (sh), 945 (s), 883 (sh), 875 (s), 812 (vs), 773 (s), 630 (w), 500 (m), 455 (m), 371 (m), 360 (sh), 328 (vw). Raman (cm^{-1}): 970 (vs), 942 (m), 907 (w), 628 (m), 246 (s), 213 (m), 158 (w), 107 (w) (difficult to obtain, even with the rotating-sample technique).

(E) α-$PMo_{12}O_{40}^{3-}$ (V) (Noted α-PMo_{12}). (1) α-$Na_2HPMo_{12}O_{40}\cdot14H_2O$ (Vc) (Noted α-PMo_{12}Na). Preparation:[5] To 420 mL of a 2.85 M aqueous solution of Na_2MoO_4 were added successively 6.8 mL of 85% H_3PO_4 (~14.7 M) and 284 mL of 70% $HClO_4$ (~11.7 M). The disodium salt Vc precipitated from the yellow lukewarm solution. After the mixture was cooled to room temperature, the microcrystalline powder was filtered and air-dried (250 g). Recrystallization in a mixture of 40 mL Et_2O/200 mL H_2O gave 180 g of greenish microcrystals.

Polarographic characterization: glassy carbon electrode; 0.5 M $HClO_4$ in 1:1 (v/v) water/1,4-dioxane; +0.310 V (2 F); +0.175 V (2 F); –0.065 V (2 F); –0.210 V (2 F); –0.300 V (2 F). TG: total weight loss 14.5 H_2O. IR (cm^{-1}): 1068 (s), 978 (sh), 962 (vs), 869 (s), 785 (vs), 593 (w), 495 (vw), 455 (sh), 400 (sh), 377 (s), 339 (s), 305 (vw), 275 (w), 260 (w). Raman (cm^{-1}): 995.5 (vs), 979 (w), 966.5 (m), 905.5 (m), 875 (sh), 802 (w), 665 (sh), 604 (m), 502 (w), 465 (w), 367 (w), 343 (vw), 307 (vw), 251.5 (s), 218 (w), 207 (w).

(2) α-$H_3PMo_{12}O_{40}\cdot14H_2O$ (Va) (Noted α-PMo_{12}H). Va was obtained from an aqueous solution of Vc (250 g/200 mL), acidified by 50 mL of 12 M HCl, and extracted by Et_2O (400 mL). The heavy layer (300 mL), added with half its volume of water, gave yellow crystals after desiccation (190 g).

TG: water content exptl 13.8%, calcd for 14 H_2O 13.8%; cation content exptl 1.5%, calcd for $^3/_2$ "H_2O" 1.5%. IR (cm^{-1}): 1067 (s), 975 (sh), 963 (vs), 870 (s), 810 (sh), 785 (vs), 593 (w), 500 (w), 453 (w), 400 (sh), 378 (s), 339 (m). Raman (cm^{-1}): 995.5 (vs), 980 (sh), 972 (m), 905.5 (w), 870 (sh), 675 (sh), 603.5 (m), 500 (w), 465 (w), 399 (w), 370 (w), 340 (w), 251 (s), 221.5 (w), 207.5 (w), 159 (s), 110 (s).

(3) α-$[(n\text{-}C_4H_9)_4N]_3PMo_{12}O_{40}\cdot xH_2O$ (Vk) (Noted α-PMo_{12}TBA). The preparation of Vk was published elsewhere.[3] TG: water content x = 0.8; cation content exptl 29.5%, calcd for $^3/_2$ "$(TBA)_2O$" 29.4%. IR (cm^{-1}): 1063 (s), 1030 (vw), 965 (sh), 955 (vs), 880 (s), 805 (vs), 738 (vw), 612 (w), 505 (m), 464 (w), 386 (s), 340 (m). Raman (cm^{-1}): 986 (vs), 971 (sh), 964 (m), 894 (w), 603 (m), 465 (vw), 451 (vw), 370 (vw), 255 (w), 246 (s), 215 (w), 203 (w), 169 (w), 154 (w), 109 (s), 84 (w).

(4) α-$[(n\text{-}C_6H_{13})_4N]_3PMo_{12}O_{40}$ (VI) (Noted α-PMo_{12}THA). VI was obtained from Vc in the following way: A 10-g quantity of Vc was dissolved in 20 mL of water; a 5-g quantity of (THA)Br was dissolved in 50 mL of CH_2Cl_2, and the mixture was poured into the molybdophosphate solution with vigorous stirring. Three phases were formed: a yellow solid one, a lower liquid one (CH_2Cl_2), yellow colored, and an aqueous upper one, poorly colored. The solid was washed with Et_2O, providing 8.5 g of VI. A further yield of 2.5 g was obtained by addition of Et_2O to the CH_2Cl_2 phase. Recrystallization was performed in CH_2Cl_2.

TG: anhydrous; cation content exptl 38.0%, calcd for $^3/_2$ "$(THA)_2O$" 37.6%. IR (cm^{-1}): 1062 (s), 986 (vw), 964 (sh), 954 (s), 878 (s), 803 (vs), 725 (m), 608 (w), 500 (m), 460 (w), 381 (s), 338 (m), 258 (m). Raman (cm^{-1}): 986 (vs), 965.5 (m), 894 (m), 818 (vw), 773 (vw), 660 (w), 601 (m), 500 (w), 465 (w), 400 (w), 370 (w), 342 (vw), 280 (vw), 247 (s), 215 (w), 202.5 (w), 167 (sh), 153 (s), 108 (s), 82 (sh).

(F) β-$PMo_{12}O_{40}^{3-}$ (VI) (Noted β-PMo_{12}). β-$[(n\text{-}C_4H_9)_4N]_3PMo_{12}O_{40}$ (VIk) (Noted β-PMo_{12}TBA). Preparation of a "Mo(V)" solution: A 140 mL quantity of a 1 M aqueous solution of Na_2MoO_4 was acidified by 130 mL of aqueous concentrated HCl (~12 M). The solution was diluted to 400 mL with water; 350 mL of this solution was put in the cathodic compartment of the electrolysis cell, and the other 50 mL, in the anodic compartment. Electrolysis was performed under N_2 on a Pt electrode, at a controlled potential of –0.2 V vs. SCE. The obtained cathodic solution was stored under Ar. The Mo(V) concentration and free acidity were determined by redox and protometric titrations, respectively (["Mo(V)"] = 0.35 M; [H_3O^+] = 3.7 M) (for our purpose, the exact nature of the "Mo(V)" species is not of relevance).

Synthesis of the four-electron-reduced molybdophosphate species (β-IV) (performed under N_2): A 15-mL quantity of 1 M aqueous H_3PO_4 was added to 200 mL of the "Mo(V)" solution. Then 60 mL of degassed aqueous 2 M Na_2MoO_4 solution was poured in dropwise with stirring; the solution turned blue. The flask was securely stoppered and stored on a water bath (~60 °C) overnight, which allows complete α-IV → β-IV isomerization. After the mixture was cooled to room temperature, the acid was precipitated by 160 mL of aqueous concentrated HCl (~12 M), allowed to deposit in the refrigerator, and filtered. The dark blue solid was quickly washed several times by small quantities of aqueous concentrated HCl in order to remove the adsorbed Mo(V) species. Drying in vacuo over NaOH and P_2O_5 yielded 17 g of β-IV ($H_7PMo_{12}O_{40}\cdot xH_2O$), as shown by titration.

Preparation of the nonreduced compound (β-O): A 7-g quantity of the reduced form (β-IV) was slowly added by small quantities into a mixture of 60 mL of CH_3CN and 1 mL of aqueous concentrated HNO_3 (~13 M). The blue solution turned yellow, and the nondissolved white residue was filtered off. The filtrate was precipitated by 10 g of solid (TBA)Br. The orange-yellow solid was filtered and washed several times by anhydrous Et_2O. For purification (especially to remove $(TBA)Br_3$), the crude product was dissolved again in anhydrous CH_3CN and reprecipitated by dry Et_2O; this procedure yielded 5.1 g of VIk, free of the α form, as shown by polarography.

Polarographic characterization: Pt electrode; 0.5 M $HClO_4$ in 1:1 (v/v) water/1,4-dioxane; +0.420 V (2 F); +0.360 V (2 F); –0.120 V (2 F). TG: anhydrous; cation content exptl 29.5%, calcd for $^3/_2$ "$(TBA)_2O$" 29.4%. IR (cm^{-1}): 1056 (s), 987 (sh), 965 (sh), 953 (s), 882 (m), 863 (m), 804 (vs), 738 (w), 595 (vw), 488 (w), 401 (sh), 378 (m), 371 (m), 339 (m). Raman (cm^{-1}): 988 (vs), 968 (m), 950 (sh), 885 (w), 605 (m), 363 (vw), 300 (vw), 244 (s), 140 (w).

(G) α-$AsMo_{12}O_{40}^{3-}$ (VII) (Noted α-$AsMo_{12}$). (1) α-$Li_3AsMo_{12}O_{40}.xH_2O$ (VIIb) (Noted α-$AsMo_{12}$Li). The preparation of VIIb was published elsewhere.[3]

Polarographic characterization: glassy carbon electrode; 0.5 M $HClO_4$ in 1:1 (v/v) water/1,4-dioxane; +0.330 V (2 F); +0.215 V (2 F), –0.010 V (2 F); –0.155 V (2 F); –0.250 V (2 F). TG: total weight loss (no well-defined intermediary plateau) corresponds to 26.6 H_2O + $^1/_2$ As_2O_5. IR (cm^{-1}): 987 (sh), 969 (sh), 963 (s), 906 (sh), 895 (s), 846 (m), 773 (vs), 572 (vw), 515 (vw), 469 (w), 450 (sh), 369 (s), 330 (m). Raman (cm^{-1}): 993.5 (s), 976 (m), 875 (w), 605 (m), 250 (s) (difficult to obtain, even with the rotating-sample technique).

(2) α-$[(n\text{-}C_4H_9)_4N]_3AsMo_{12}O_{40}\cdot xH_2O$ (VIIk) (Noted α-$AsMo_{12}$TBA). The preparation of VIIk was published elsewhere.[3]

TG: water content x = 0.9; second weight loss exptl 33.4%, calcd for $^3/_2$ "$(TBA)_2O$" + $^1/_2$ As_2O_5 33.4%. IR (cm^{-1}): 980 (sh), 965 (s), 895 (vs), 855 (m), 790 (vs), 740 (vw), 608 (w), 498 (m), 470 (m), 453 (m), 379 (s), 330 (w). Raman (cm^{-1}): 986 (vs), 968 (sh), 961 (m), 880 (w), 773 (vw), 655 (w), 602 (m), 488 (vw), 454 (vw), 397 (vw), 385 (vw), 360 (w), 247 (s), 230 (vw), 214 (m), 203 (m), 157 (m), 112 (s), 83 (m).

(H) β-$AsMo_{12}O_{40}^{3-}$ (VIII) (Noted β-$AsMo_{12}$). β-$[(n\text{-}C_4H_9)_4N]_3AsMo_{12}O_{40}\cdot xH_2O$ (VIIIk) (Noted β-$AsMo_{12}$TBA). Synthesis of the four-electron-reduced species according to Contant's procedure[6] modified as follows: The synthesis was performed under N_2. A 50-mL quantity of a 0.5 M disodium arsenate aqueous solution was added to 300 mL of a 0.35 M "Mo(V)" solution prepared as above (see preparation of VIk). Then 100 mL of a degassed aqueous 2 M Na_2MoO_4 solution was poured in dropwise, with stirring. The solution turned blue. After addition of 160 mL of aqueous concentrated HCl (~12 M), the solution was stored overnight in the refrigerator. The dark blue crystals were then treated as in the preparation of the parent phosphorus compound (VIk) to get β-IV ($H_7AsMo_{12}O_{40}\cdot xH_2O$).

Preparation of the nonreduced compound (β-O): A 7-g quantity of the reduced form (β-IV) was slowly poured, by small quantities, into a mixture of 60 mL of CH_3CN and 2 mL of aqueous concentrated HNO_3 (~13 M). The blue solution quickly turned yellow. Addition of 10 g of solid (TBA)Br induced the precipitation of VIIIk as an orange-yellow solid, which was filtered and washed several times with anhydrous Et_2O (yield 7.4 g).

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Polarographic characterization: glassy carbon electrode; 0.5 M HCl in 40:60 (v/v) water/1,4-dioxane; +0.430 V (2 F); +0.370 V (2 F); −0.030 V (2 F). TG: water content $x = 1.6$; second weight loss exptl 33.3%, calcd for $^3/_2$ "$(TBA)_2O$" + $^1/_2$ As_2O_5 33.4%. IR (cm^{-1}): 980 (sh), 965 (s), 890 (vs), 788 (vs), 740 (sh), 610 (vw), 495 (w), 462 (w), 442 (sh), 375 (m), 361 (m), 335 (vw), 325 (vw). Raman (cm^{-1}): 987 (s), 965 (m), 959 (sh), 893 (w), 862 (w), 821 (w), 675 (w), 608 (m), 392 (vw), 244.5 (m), 201 (vw), 154 (w).

(I) α-$BW_{12}O_{40}{}^{5-}$ (IX) (Noted α-BW_{12}). (1) α-$K_5BW_{12}O_{40}\cdot xH_2O$ (IXd) (Noted α-$BW_{12}K$). IXd was prepared according to Copaux's method[7] modified by Hervê and Têzê as follows: To 100 mL of water were added successively with vigorous stirring 100 g of $Na_2WO_4\cdot 2H_2O$, 5 g of boric acid (H_3BO_3), and 60 mL of aqueous 6 M HCl. The solution (pH ~6) was allowed to boil for many hours (water was added from time to time). The solid B paratungstate $Na_{10}W_{12}O_{41}\cdot xH_2O$ (17 g) was filtered off; the filtrate was acidified by aqueous 6 M HCl to pH 2 and allowed to boil for $^1/_2$ h, and precipitation was effected by 20 g of solid KCl. After filtration and washing with Et_2O, 71 g of crude product was obtained and recrystallized in 50 mL of water at 60 °C (yield 57 g).

Polarographic characterization: dropping-mercury electrode; aqueous 1 M CH_3COOH/1 M CH_3COONa buffer; −0.50 V (2 F); −0.72 V (2 F). TG: very low heating rate to avoid overflowing of the material during dehydration; water content $x = 11.4$. IR (cm^{-1}): 1003 (w), 960 (s), 910 (s), 807 (vs), 610 (vw), 585 (sh), 505 (m), 470 (sh), 425 (w), 379 (s), 335 (s), 285 (w). Raman (cm^{-1}): 981.5 (vs), 961.5 (m), 912 (m), 844 (w), 772 (w), 610 (vw), 536 (w), 474 (vw), 401 (w), 343 (w), 296 (w), 240 (m), 212 (s), 193 (w), 153 (s), 91 (sh), 82 (s).

(2) α-$[(n\text{-}C_4H_9)_4N]_4HBW_{12}O_{40}\cdot xH_2O$ (IXk) (Noted α-$BW_{12}TBA$). IXk was precipitated from a 0.02 M aqueous solution of IXd by addition of a saturated aqueous solution of (TBA)Br. The solid was washed successively with water, EtOH, and Et_2O. This crude product was suspended in hot water in which the potassium salt IXd dissolved and could be filtered off; this treatment of the crude product was performed several times until complete elimination of IXd. IXk was then dissolved in CH_3CN and reprecipitated by Et_2O.

TG: water content $x = 4.5$; cation content exptl 26.5%, calcd for 2 "$(TBA)_2O$" + $^1/_2$ "H_2O" 26.4%. IR (cm^{-1}): 990 (vw), 985 (vw), 950 (s), 900 (s), 817 (vs), 750 (sh), 610 (vw), 530 (m), 508 (m), 475 (sh), 421 (w), 384 (s), 340 (m), 287 (w). Raman (cm^{-1}): 971 (vs), 951 (m), 942 (sh), 908 (m), 775 (w), 538 (w), 477 (vw), 383 (vw), 372 (vw), 341 (vw), 293 (w), 243 (m), 210 (s), 197 (w), 185 (w), 152 (sh), 148 (s), 92 (s), 80 (m).

(J) α-$SiW_{12}O_{40}{}^{4-}$ (X) (Noted α-SiW_{12}). (1) α-$H_4SiW_{12}O_{40}\cdot xH_2O$ (Xa) (Noted α-$SiW_{12}H$). The preparation of Xa was described elsewhere.[8]

Polarographic characterization: dropping-mercury electrode; aqueous 1 M CH_3COOH/1 M CH_3COONa buffer; −0.260 V (1 F); −0.520 V (1 F); −0.950 V (2 F). TG: water content $x = 19$; cation content exptl 1.2%, calcd for 2 "H_2O" = 1.2%. IR (cm^{-1}): 1020 (w), 981 (s), 928 (vs), 880 (m), 785 (vs), 552 (sh), 540 (m), 475 (w), 415 (w), 373 (s), 332 (s), 275 (w). Raman (cm^{-1}): 1016 (w), 1000 (vs), 975 (m), 923 (w), 880 (vw), 551 (w), 538 (w), 458 (vw), 398 (vw), 328 (vw), 237 (m), 222 (m), 207 (m), 174.5 (m), 154 (s), 103 (s), 87 (s).

(2) α-$K_4SiW_{12}O_{40}\cdot xH_2O$ (Xd) (Noted α-$SiW_{12}K$). Xd was obtained by partial neutralization (pH <2) of a saturated aqueous solution of Xa by about 0.1 M aqueous KOH. Recrystallization was performed in water.

TG: efflorescent; water content $x = 4.8$. IR (cm^{-1}): 1020 (w), 999 (sh), 980 (s), 940 (sh), 925 (vs), 894 (m), 878 (m), 780 (vs), 550 (sh), 530 (m), 474 (w), 413 (w), 373 (s), 333 (s), 275 (m), 265 (sh). Raman (cm^{-1}): 1019 (w), 995 (vs), 984.5 (m), 966 (sh), 900 (w), 558 (w), 401 (vw), 340 (vw), 289 (vw), 250 (m), 220.5 (s), 210 (m), 202 (vw), 161 (sh), 154.5 (m), 107 (s), 87 (m).

(3) α-$Ba_2SiW_{12}O_{40}\cdot 16H_2O$ (Xf) (Noted α-$SiW_{12}Ba$). Xf was prepared by the same method as for Xd, but with KOH replaced by $Ba(OH)_2$.

TG: water content exptl 9.1%, calcd for 16 H_2O 9.0%. IR (cm^{-1}): 1020 (w), 998 (sh), 981 (s), 925 (vs), 892 (m), 878 (m), 780 (vs), 553 (sh), 539 (m), 474 (w), 454 (sh), 413 (w), 378 (sh), 371 (s), 332 (s), 281 (m). Raman (cm^{-1}): 1016 (w), 999 (vs), 984 (sh), 969 (w), 925 (w), 880 (vw), 554 (w), 458 (vw), 333 (vw), 249 (sh), 239 (m), 223 (s), 210 (sh), 179 (w), 154.5 (s), 104 (m), 92 (s).

(4) α-$[(CH_3)_4N]_4SiW_{12}O_{40}\cdot xH_2O$ (Xh) (Noted α-$SiW_{12}TMA$). Xh was obtained by addition of a saturated solution of (TMA)Cl to a saturated solution of Xa. Recrystallization was performed in water.

TG: water content $x = 2.1$; cation content exptl 10.4%, calcd for 2 "$(TMA)_2O$" 10.3%. IR (cm^{-1}): 1015 (m), 975 (s), 950 (sh), 920 (vs), 882 (m), 790 (vs), 745 (sh), 550 (sh), 533 (m), 515 (sh), 480 (w), 455 (sh), 420 (w), 382 (s), 333 (m), 315 (sh), 280 (m). Raman (cm^{-1}): 1012 (w), 992 (vs), 982 (sh), 971.5 (m), 952 (w), 907 (w), 887 (w), 752 (w), 582 (sh), 537 (w), 457 (w), 331 (w), 311 (w), 288 (w), 261 (w), 242.5 (m), 233.5 (m), 221 (s), 207 (m), 177 (w), 157.5 (m), 149 (s), 104.5 (s), 93 (sh).

(5) α-$[(n\text{-}C_4H_9)_4N]_4SiW_{12}O_{40}$ (Xk) (Noted α-$SiW_{12}TBA$). Xk was prepared by the same method as for Xh, replacing (TMA)Cl by (TBA)Br. It was recrystallized from a CH_3CN/Et_2O mixture.

TG: anhydrous; cation content exptl 25.9%, calcd for 2 "$(TBA)_2O$" 26.0%. IR (cm^{-1}): 1011 (m), 967 (s), 920 (vs), 883 (m), 797 (vs), 552 (sh), 542 (m), 515 (sh), 479 (w), 419 (vw), 383 (s), 334 (m), 281 (m). Raman (cm^{-1}): 1009 (w), 987 (vs), 966 (s), 924 (w), 906 (m), 886 (w), 560 (sh), 533 (m), 376 (w), 334 (vw), 288 (w), 244.5 (m), 218.5 (s), 210.5 (sh), 187 (w), 157.5 (s), 149.5 (s), 102.5 (s), 89 (s).

(K) β-$SiW_{12}O_{40}{}^{4-}$ (XI) (Noted β-SiW_{12}). (1) β-$K_4SiW_{12}O_{40}\cdot 9H_2O$ (XId) (Noted β-$SiW_{12}K$). XId was prepared according to Hervê–Têzê procedure[9] modified as follows: To 300 mL of a 2 M aqueous solution of Na_2WO_4 was added 240 mL of 3 M aqueous HCl by fractions with vigorous stirring in order to redissolve the local precipitate of tungstic acid. Then 100 mL of a 0.5 M aqueous solution of sodium metasilicate was quickly added. A 6 M aqueous HCl (~20 mL) solution was added to reach pH 5.5. After standing $^1/_2$ h, the solution was mixed quickly with another fraction of 6 M HCl (total 6 M HCl added 60 mL; final pH ~1). After concentration to about 400 mL, the solution was filtered to remove unreacted silica. The pH was adjusted to about 2 with aqueous 1 M KOH. Addition of solid KCl (50 g) induced the precipitation of XId, which was filtered and dried in air without preliminary washing. Recrystallization at room temperature from an aqueous solution saturated at 50 °C (pH adjusted to 2 by HCl) gave 110 g of large blocks of pure XId: the nondissolved α isomer was preliminarily filtered from the warm solution.

Polarographic characterization: dropping-mercury electrode; aqueous 1 M CH_3COOH/1 M CH_3COONa buffer; −0.140 V (1 F); −0.390 V (1 F); −0.740 V (2 F). TG: water content exptl 5.0%, calcd for 9 H_2O 5.0%. IR (cm^{-1}): 1018 (w), 984 (s), 917 (vs), 865 (vw), 791 (vs), 550 (sh), 530 (m), 510 (sh), 427 (w), 395 (sh), 372 (sh), 360 (s), 335 (s), 285 (w). Raman (cm^{-1}): 1015 (vw), 999 (vs), 983 (m), 920 (w), 872 (w), 551 (w), 250 (w), 231 (w), 214.5 (s), 205 (sh), 170 (sh), 161.5 (w), 142 (w), 121 (w), 105 (m), 85 (w), 75 (m).

(2) β-$H_4SiW_{12}O_{40}\cdot xH_2O$ (XIa) (Noted β-$SiW_{12}H$). XIa was obtained from a saturated aqueous solution of XId acidified and treated as in the preparation for Ia.

TG: water content $x = 17.5$; cation content exptl 1.2%, calcd for 2 "H_2O" 1.2%. IR (cm^{-1}): 1018 (w), 980 (s), 920 (vs), 790 (vs), 550 (sh), 530 (m), 510 (sh), 427 (w), 395 (sh), 372 (sh), 360 (s), 335 (s), 285 (w). Raman (cm^{-1}): 1016 (vw), 999 (vs), 983 (m), 913 (w), 890 (w), 868 (w), 588 (vw), 555 (w), 400 (vw), 340 (vw), 304 (vw), 243 (m), 213.5 (s), 193 (w), 167 (w), 155 (w), 138 (s), 115.5 (m), 102.5 (s), 83 (w), 73.5 (m).

(3) β-$[C(NH_2)_3]_4SiW_{12}O_{40}\cdot xH_2O$ (XIe) (Noted β-$SiW_{12}Gua$). XIe was precipitated from a 0.01 M aqueous solution of XId by a saturated aqueous solution of (Gua)Cl. The crude product was recrystallized from water.

TG: water content $x = 2$; cation content exptl 8.8%, calcd for 2 "$(Gua)_2O$" 8.7%. IR (cm^{-1}): 1017 (w), 980 (s), 917 (vs), 865 (w), 790 (vs), 550 (sh), 525 (m), 490 (sh), 430 (w), 395 (sh), 378 (sh), 370 (s), 337 (s), 289 (w), 275 (w). Raman (cm^{-1}): 1010 (w), 994 (vs), 978 (m), 971 (sh), 915 (w), 895 (w), 870 (w), 554 (w), 400 (vw), 238 (m), 211 (s), 189 (w), 166 (sh), 159 (w), 140 (s), 115 (m), 102 (m).

(4) β-$(NH_4)_4SiW_{12}O_{40}\cdot xH_2O$ (XIg) (Noted β-$SiW_{12}NH_4$). XIg was obtained by partial neutralization (pH <2) of a saturated aqueous solution of XIa by 1 M aqueous ammonia solution.

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(9) Têzê, A.; Hervê, G. *J. Inorg. Nucl. Chem.* **1977**, *39*, 999.

TG: water content $x = 6.2$; cation content exptl 3.5%, calcd for 2 “$(NH_4)_2O$” 3.5%. IR (cm^{-1}): 1015 (m), 979 (s), 915 (s), 855 (vw), 785 (s), 548 (m), 528 (m), 508 (sh), 425 (w), 395 (m), 370 (sh), 355 (m), 330 (s). Raman (cm^{-1}): 1015 (vw), 995 (vs), 974 (m), 925 (vw), 903 (vw), 878 (w), 834 (vw), 556 (w), 399 (vw), 344 (vw), 245 (sh), 213 (s), 189 (w), 173 (w), 162 (vw), 158 (vw), 138 (m), 131 (w), 125 (w), 112 (m), 107 (w), 103 (m).

(5) β-$[(CH_3)_4N]_4SiW_{12}O_{40}\cdot xH_2O$ (XIh) (Noted β-SiW_{12}TMA). The same preparation as for XIe was used, replacing (Gua)Cl by (TMA)Cl. Recrystallization was performed from water.

TG: water content $x = 2.2$; cation content exptl 10.3%, calcd for 2 “$(TMA)_2O$” 10.3%. IR (cm^{-1}): 1015 (w), 976 (s), 948 (sh), 915 (vs), 870 (w), 790 (vs), 610 (vw), 555 (sh), 533 (m), 515 (sh), 460 (sh), 430 (w), 402 (m), 378 (m), 365 (sh), 340 (s), 302 (vw), 286 (w), 272 (w). Raman (cm^{-1}): 1007 (w), 991.5 (vs), 974 (m), 953 (w), 890 (w), 878 (w), 753 (w), 553 (w), 538 (w), 455 (vw), 368 (vw), 268 (w), 250 (w), 240 (w), 228 (w), 217.5 (m), 209 (s), 202 (sh), 187.5 (w), 166 (w), 155.5 (w), 138 (s), 116.5 (s), 105 (s), 84 (m), 75 (m).

(6) β-$[(C_2H_5)_4N]_4SiW_{12}O_{40}\cdot xH_2O$ (XIi) (Noted β-SiW_{12}TEA). An approximately 0.01 M aqueous solution of XId was precipitated by a saturated aqueous solution of (TEA)Br. The wet precipitate was suspended in warm water, a small amount of (TEA)Br solution was added, and the mixture was filtered again. This operation was performed many times until complete elimination of the potassium salt. Adsorbed water was removed by washing with MeOH and Et_2O. Recrystallization was performed from a CH_3CN/Et_2O mixture.

TG: water content $x = 1.0$; cation content exptl 16.2%, calcd for 2 “$(TEA)_2O$” 16.3%. IR (cm^{-1}): 1011 (m), 973 (s), 915 (vs), 870 (w), 793 (vs), 610 (vw), 554 (sh), 535 (m), 512 (sh), 429 (w), 400 (m), 378 (m), 362 (sh), 340 (m), 300 (vw), 287 (w), 262 (w). Raman (cm^{-1}): 1007 (vw), 989.5 (vs), 971 (m), 918 (sh), 913 (w), 892 (w), 878 (w), 673 (w), 663 (w), 553 (m), 536 (m), 511 (sh), 474 (vw), 456 (vw), 421 (w), 390 (vw), 343 (vw), 312 (vw), 279 (vw), 269 (w), 244 (m), 230 (m), 219 (m), 211 (s), 202 (sh), 187 (w), 167.5 (w), 155 (w), 137 (s), 117 (m), 103.5 (s), 85 (m), 74.5 (m).

(7) β-$[(n\text{-}C_3H_7)_4N]_4SiW_{12}O_{40}\cdot xH_2O$ (XIj) (Noted β-SiW_{12}TPA). XIj had the same preparation and purification procedure as for XIi, using (TPA)Br instead of (TEA)Br.

TG: water content $x = 1.3$; cation content exptl 21.4%, calcd for 2 “$(TPA)_2O$” 21.4%. IR (cm^{-1}): 1010 (w), 970 (s), 913 (vs), 870 (w), 800 (vs), 765 (sh), 610 (vw), 553 (sh), 533 (w), 512 (sh), 429 (w), 400 (m), 380 (m), 362 (sh), 340 (m), 300 (vw), 288 (w), 272 (w). Raman (cm^{-1}): 1006 (vw), 989 (vs), 969 (m), 913 (w), 890.5 (w), 877 (w), 848 (vw), 552 (w), 536 (w), 510 (sh), 464 (vw), 456 (vw), 428 (vw), 403 (vw), 370 (w), 349 (w), 333 (w), 307 (w), 278 (w), 268 (w), 240 (m), 219 (sh), 210 (s), 202 (sh), 188 (w), 168.5 (w), 155.5 (w), 148.5 (w), 137.5 (s), 116 (m), 85 (m), 73 (m).

(8) β-$[(n\text{-}C_4H_9)_4N]_4SiW_{12}O_{40}$ (XIk) (Noted β-SiW_{12}TBA). XIk had the same preparation and purification procedure as XIi, by replacing (TEA)Br by (TBA)Br.

TG: anhydrous; cation content exptl 26.2%, calcd for 2 “$(TBA)_2O$” 26.0%. IR (cm^{-1}): 1009 (w), 969 (s), 914 (vs), 870 (w), 809 (vs), 793 (vs), 735 (sh), 608 (vw), 551 (sh), 532 (w), 510 (sh), 425 (w), 399 (m), 378 (m), 360 (sh), 337 (m), 295 (vw), 285 (w). Raman (cm^{-1}): 1003 (w), 988.5 (vs), 968.5 (m), 909 (w), 891 (w), 878 (w), 554 (w), 536 (w), 343 (w), 309 (vw), 267 (w), 242 (m), 221 (m), 210 (s), 189 (w), 168 (w), 155 (w), 138 (s), 117 (m), 103.5 (s), 84.5 (w), 73 (m).

(9) β-$[(n\text{-}C_6H_{13})_4N]_4SiW_{12}O_{40}$ (XIl) (Noted β-SiW_{12}THA). XIl was prepared from XId in the following way: A 10-g sample of XId was dissolved in 20 mL of water, at 40 °C, and 5 g of (THA)Br was emulsified in 30 mL of warm water. The first solution was slowly poured into the second one; a gelatinous precipitate was formed. After addition of 25 mL of 1,4-dioxane, the precipitate was allowed to peptize for $^1/_2$ h at 40 °C. It was then filtered and washed with water, 1,4-dioxane, and Et_2O, yielding 12.5 g of crude product. The latter was very soluble in CH_2Cl_2 but could not be crystallized from its solution.

TG: anhydrous; cation content exptl 33.8%, calcd for 2 “$(THA)_2O$” 33.8%. IR (cm^{-1}): 1010 (m), 987 (sh), 969 (s), 914 (s), 868 (m), 810 (vs), 790 (vs), 725 (sh), 550 (m), 530 (m), 507 (m), 425 (w), 398 (s), 377 (s), 359 (m), 336 (s), 296 (w), 284 (w). Raman (cm^{-1}): 1003 (w), 988.5 (vs), 969 (m), 918 (w), 893 (w), 877 (w), 817 (vw), 554 (w), 535 (w), 335 (vw), 270 (vw), 243 (w), 231 (vw), 220 (w), 211 (m), 202 (w), 188 (w), 168 (w), 155 (sh), 148 (sh), 143 (m), 137.5 (s), 116.5 (m), 103 (s), 84 (w), 73 (w).

(L) α-$GeW_{12}O_{40}{}^{4-}$ (XII) (Noted α-GeW_{12}). (1) α-$H_4GeW_{12}O_{40}\cdot 14H_2O$ (XIIa) (Noted α-GeW_{12}H). A 250-mL quantity of a 1.25 M aqueous solution of Na_2WO_4 was mixed with 70 mL of the germanate stock solution (see part C) and the mixture was warmed to 80 °C. Concentrated (~13 M) aqueous HNO_3 (~45 mL) was added dropwise with stirring until pH 0.5 (cloudiness that appeared at the beginning of the addition progressively dissolved, and the solution became clear at pH 5). After storage for 1 h at 80 °C to complete $\beta \rightarrow \alpha$ isomerization, the solution was cooled at room temperature. A further addition of 10 mL of 13 M HNO_3 allowed the extraction by Et_2O. The colorless heavy layer was treated as in the synthesis of Ia. Crystallization was performed in the refrigerator (yield 66 g).

Polarographic characterization: dropping-mercury electrode; aqueous 1 M CH_3COOH/1 M CH_3COONa buffer; –0.200 V (1 F); –0.460 V (1 F); –0.890 V (2 F). TG: water content exptl 8.9%, calcd for 14 H_2O 8.6%; cation content exptl 1.2%, calcd for 2 “H_2O” 1.2%. IR (cm^{-1}): 980 (s), 903 sh), 883 (s), 818 (sh), 760 (vs), 645 (sh), 529 (m), 461 (m), 369 (s), 347 (m), 323 (m), 265 (sh), 247 (w). Raman (cm^{-1}): 1001 (vs), 974.5 (m), 911 (w), 888 (w), 571 (sh), 548 (w), 453 (vw), 321 (vw), 244 (m), 238 (m), 226 (s), 205.5 (m), 190 (w), 170 (m), 156 (s), 115 (sh), 108 (s), 89 (s), 76 (w), 64 (w).

(2) α-$K_4GeW_{12}O_{40}\cdot xH_2O$ (XIId) (Noted α-GeW_{12}K). XIId was obtained by addition of a 1 M aqueous solution of K_2CO_3 to a saturated aqueous solution of XIIa. Recrystallization was performed in water.

TG: water content $x = 7.0$. IR (cm^{-1}): 979 (s), 880 (s), 823 (sh), 769 (vs), 527 (m), 462 (m), 372 (s), 347 (m), 323 (m). Raman (cm^{-1}): 991.5 (vs), 971 (s), 908 (w), 887 (m), 834 (vw), 550 (w), 450 (vw), 440 (vw), 397 (w), 361 (w), 245 (m), 221.5 (s), 205 (s), 155 (s), 115 (sh), 105 (s), 89 (s), 75 (sh).

(3) α-$[(n\text{-}C_4H_9)_4N]_4GeW_{12}O_{40}$ (XIIk) (Noted α-GeW_{12}TBA). XIIk was obtained from XIId and purified by using the same procedure as for IXk.

TG: anhydrous; cation content exptl 25.9%, calcd for 2 “$(TBA)_2O$” 25.7%. IR (cm^{-1}): 965 (s), 895 (sh), 885 (vs), 830 (vs), 780 (vs), 535 (m), 465 (s), 412 (w), 380 (s), 358 (sh), 325 (w). Raman (cm^{-1}): 986 (vs), 964 (m), 895 (m), 567 (m), 538 (m), 521 (sh), 359 (w), 242 (s), 235 (s), 221 (s), 208 (s), 172 (w), 159 (sh), 152 (s), 106 (s), 90 (s).

(M) β-$GeW_{12}O_{40}{}^{4-}$ (XIII) (Noted β-GeW_{12}). (1) β-$K_4GeW_{12}O_{40}\cdot xH_2O$ (XIIId) (Noted β-GeW_{12}K). A 30-mL quantity of a 2 M aqueous solution of Na_2WO_4 was acidified by 12 mL of aqueous 6 M HCl; addition was performed slowly with vigorous stirring in order to redissolve the local precipitate of tungstic acid. A 10-mL quantity of a fresh germanate solution (prepared as in the synthesis of IIIa but more concentrated; [Ge] = 0.5 M) was acidified by 2 mL of 6 M aqueous HCl. The resulting white colloid was quickly poured into the tungstate solution (final pH ~6.5). The beaker that had contained the germanate was washed by 6 mL of 6 M HCl, which dissolved the colloid left; the clear solution obtained was added to the tungstate solution (final pH ~1). XIIId was precipitated by addition of 15 g of solid KCl. The white precipitate was filtered, washed with Et_2O, and air-dried (yield 6.5 g).

Polarographic characterization: dropping-mercury electrode; aqueous 1 M CH_3COOH/1 M CH_3COONa buffer; –0.110 V (1 F); –0.350 V (1 F); –0.700 V (2 F). TG: water content $x = 9.4$. IR (cm^{-1}): 980 (s), 895 (s), 828 (vs), 775 (vs), 530 (m), 463 (s), 425 (w), 390 (sh), 380 (sh), 360 (s), 320 (w). Raman (cm^{-1}): 999 (vs), 982 (m), 905 (w), 862 (w), 546 (w), 249 (m), 230 (m), 217 (s), 211 (m), 190 (sh), 162 (w), 144 (m), 123 (m), 107 (s), 87 (w), 75 (m).

(2) β-$H_4GeW_{12}O_{40}\cdot xH_2O$ (XIIIa) (Noted β-GeW_{12}H). XIIIa was obtained from a saturated aqueous solution of XIIId acidified and treated as in the synthesis of Ia.

TG: water content $x = 22.0$; cation content exptl 1.2%, calcd for 2 “H_2O” 1.2%. IR (cm^{-1}): 980 (s), 922 (sh), 895 (s), 825 (s), 775 (vs), 530 (m), 455 (m), 425 (w), 380 (sh), 355 (s), 335 (sh). Raman (cm^{-1}): 999 (vs), 979 (m), 902 (w), 866 (w), 549 (w), 450 (vw), 319 (vw), 241 (sh), 218 (s), 195 (m), 166 (m), 157.5 (m), 140 (m), 116 (m), 105.5 (s), 83 (sh), 74.5 (s).

(3) β-$[(n\text{-}C_4H_9)_4N]_4GeW_{12}O_{40}$ (XIIIk) (Noted β-GeW_{12}TBA). XIIIk was obtained from XIIId and purified by using the same procedure as for IXk.

TG: anhydrous; cation content exptl 25.9%, calcd for 2 “$(TBA)_2O$” 25.7%. IR (cm^{-1}): 967 (s), 890 (s), 875 (sh), 830 (vs), 780 (vs), 610 (w), 538 (m), 462 (s), 420 (w), 391 (s), 380 (s), 362 (s), 335 (sh). Raman (cm^{-1}): 986.5 (vs), 964.5 (m), 906 (sh), 895 (w), 864 (w), 543 (w), 269 (w), 247 (sh), 235 (m), 220.5 (m), 212 (s), 197 (m), 188 (w), 166 (w), 156.5 (m), 140 (s), 120 (m), 117 (sh), 105.5 (s), 85.5 (m), 74 (m).

(N) α-$PW_{12}O_{40}^{3-}$ (XIV) (Noted α-PW_{12}). (1) α-$H_3PW_{12}O_{40}\cdot6H_2O$ (XIVa) (Noted α-PW_{12}H). The preparation of XIVa was described elsewhere.[10]

Polarographic characterization: dropping-mercury electrode; 1 M $LiClO_4$ in EtOH; −0.290 V (1 F); −0.470 V (1 F); −0.620 V (2 F); −0.900 V (2 F). TG: water content exptl 4.0%, calcd for 6 H_2O 3.7%; cation content exptl 0.9%, calcd for $^3/_2$ "H_2O" 1.0%. IR (cm^{-1}): 1080 (s), 990 (sh), 982 (s), 890 (s), 810 (vs), 597 (w), 527 (m), 480 (sh), 425 (w), 381 (s), 336 (m), 257 (m). Raman (cm^{-1}): 1007 (vs), 992 (m), 983.5 (m), 904 (w), 571 (vw), 546 (vw), 521 (w), 473 (vw), 418 (vw), 375 (vw), 236.5 (m), 217.5 (s), 204.5 (m), 193 (w), 177.5 (w), 159.5 (w), 150.5 (m), 101.5 (s), 92.5 (s), 81.5 (w).

(2) α-$Na_3PW_{12}O_{40}\cdot xH_2O$ (XIVc) (Noted α-PW_{12}Na). The preparation of XIVc was described elsewhere.[10]

TG: hygroscopic; water content $x = 12.0$. IR (cm^{-1}): 1081 (s), 995 (sh), 982 (s), 922 (m), 900 (m), 805 (vs), 592 (w), 522 (sh), 505 (m), 485 (sh), 380 (s), 334 (m), 256 (m). Raman (cm^{-1}): 1012.5 (vs), 992.5 (m), 987.5 (sh), 938 (w), 907 (vw), 889 (vw), 820 (vvw), 690 (vvw), 580 (vw), 542 (w), 525 (m), 505 (sh), 477 (vw), 434 (vw), 416 (vw), 398 (vw), 380 (vw), 338 (vw), 313 (vw), 242 (sh), 234 (m), 218 (s), 207 (sh), 199 (w), 159 (m), 135 (m), 116 (sh), 101 (s), 88 (s).

(3) α-$[(n\text{-}C_4H_9)_4N]_3PW_{12}O_{40}$ (XIVk) (Noted α-PW_{12}TBA). XIVk was obtained from XIVc and purified by using the same procedure as for IXk.

TG: anhydrous; cation content exptl 20.9%, calcd for $^3/_2$ "$(TBA)_2O$" 20.8%. IR (cm^{-1}): 1080 (s), 1025 (w), 987 (sh), 976 (s), 895 (s), 810 (vs), 735 (sh), 657 (sh), 596 (w), 522 (m), 511 (m), 387 (s), 375 (sh), 335 (m), 268 (sh), 250 (m). Raman (cm^{-1}): 1003.5 (vs), 993 (m), 986 (m), 925 (sh), 918.5 (w), 898 (w), 523 (w), 518 (m), 474 (w), 433 (w), 412 (w), 375 (w), 337 (w), 313 (w), 260 (w), 238.5 (sh), 231 (m), 215.5 (s), 207 (w), 186.5 (w), 155.5 (m), 142.5 (s), 100.5 (s), 87 (s).

(O) α-$AsW_{12}O_{40}^{3-}$ (XV) (Noted α-AsW_{12}). (1) α-$Na_3AsW_{12}O_{40}\cdot xH_2O$ (XVc) (Noted α-AsW_{12}Na). XVc was prepared according to Contant and Fournier's procedure in the following way: A 20-mL quantity of an ~2 M aqueous sodium arsenate solution (prepared with 5.42 g of $3As_2O_5\cdot5H_2O$ and 3.3 g of NaOH pellets) was poured into a mixture of 100 mL of water and 165 g (0.5 mol) of $Na_2WO_4\cdot2H_2O$ (only partially dissolved). A 100-mL quantity of 1,4-dioxane was added, and the paste obtained was slowly acidified by 25 mL of concentrated (~12 M) aqueous HCl with vigorous triturating. The mixture progressively fluidized and turned into a white solid suspension to which was further added 150 mL of concentrated HCl in small quantities. The stirring was continued for $^1/_2$ h. The precipitate was filtered, washed with 1,4-dioxane and Et_2O, and air-dried (yield 120 g).

Polarographic characterization: dropping-mercury electrode; 0.5 M HCl in 1:1 (v/v) water/ethanol; −0.270 V (1 F); −0.420 V (1 F); −0.580 V (2 F). TG: total weight loss (no well-defined intermediary plateau) corresponds to 26.5 H_2O + $^1/_2$ As_2O_5. IR (cm^{-1}): 987 (s), 911 (s), 872 (m), 781 (vs), 611 (w), 522 (m), 469 (m), 376 (s), 349 (sh), 329 (m). Raman (cm^{-1}): 1004 (vs), 989 (m), 915 (w), 853 (vw), 838 (w), 535 (w), 490 (vw), 348 (vw), 317 (vw), 251 (vw), 233.5 (m), 220 (s), 203.5 (s), 194 (vw), 177 (w), 161 (m), 152 (m), 146 (s), 103 (s), 89.5 (s).

(2) α-$[(n\text{-}C_4H_9)_4N]_3AsW_{12}O_{40}$ (XVk) (Noted α-AsW_{12}TBA). XVk was obtained from XVc and purified by using the same procedure as for IXk.

TG: anhydrous; cation content exptl 23.4%, calcd for $^3/_2$ "$(TBA)_2O$" + $^1/_2$ As_2O_5 23.7%. IR (cm^{-1}): 983 (s), 912 (s), 873 (m), 793 (vs), 735 (sh), 620 (vw), 525 (m), 470 (m), 420 (w), 381 (s), 358 (sh), 325 (w). Raman (cm^{-1}): 1000.5 (vs), 984 (m), 919 (w), 905 (w), 877 (w), 525 (w), 360 (w), 328 (w), 267 (w), 252 (w), 220.5 (s), 206 (s), 180 (w), 161.5 (m), 156 (m), 147 (s), 104.5 (s), 90 (s).

Results and Discussion

(i) General Considerations. The α-$XM_{12}O_{40}^{n-}$ structure (Keggin structure) consists of one XO_4 tetrahedron (X = Si^{IV}, Ge^{IV}, P^V, ...) surrounded by four M_3O_{13} sets (M = Mo^{VI} or W^{VI}) formed by three edge-sharing octahedra. The M_3O_{13} sets are linked together through oxygen atoms (named O_b) (Figure 1a). The β-$XM_{12}O_{40}^{n-}$ structure derives from that of the α isomer by rotating one M_3O_{13} set by 60° about its threefold axis (Figure 1b).

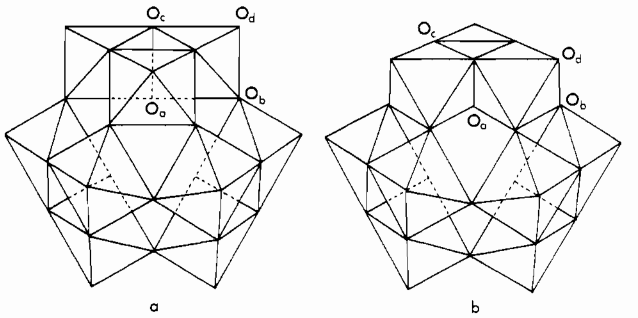

Figure 1. Coordination polyhedra as a representation of α-$XM_{12}O_{40}^{n-}$ (a) and β-$XM_{12}O_{40}^{n-}$ (b) structures (the fourth M_3O_{13} set and the XO_4 tetrahedron are not shown for clarity).

We have already developed a systematic vibrational study of polynuclear oxo complexes related to the Keggin structure.[11-13] Our study was restricted to acids and/or alkaline salts crystallized with various amounts of water molecules. We showed that intermolecular interactions such as H bonds between external oxygens and water molecules or $H_5O_2^+$ cations led to a decrease in the frequencies of the metal–oxygen stretchings. Other molecular interactions were neglected; i.e., the interpretation was discussed by assuming that each anion was isolated in the crystal lattice (zero-order approximation).

Let us recall some important assignments of the vibrational spectra of these compounds.[11,12] The XO_4 tetrahedron is assumed to vibrate almost independently from the rest of the anion. This assumption is particularly valuable for X = P^V; in the other cases, the band described as the $\nu_3(T_d)$ stretching mode of the XO_4 tetrahedron appears to be mixed with other vibrations such as M–O_b–M stretchings. The symmetric and asymmetric stretchings of the different kinds of M–O bonds are observed in the following spectral regions: M–O_d bonds (1000–960 cm^{-1}), M–O_b–M bridges ("inter" bridges between corner-sharing octahedra) (890–850 cm^{-1}), M–O_c–M bridges ("intra" bridges between edge-sharing octahedra, i.e., inside a M_3O_{13} set) (800–760 cm^{-1}). Only the M–O_d stretchings can be considered as pure vibrations: the stretchings involving O_b or O_c atoms present some bend character. This can be assumed from geometrical considerations and has been confirmed by a normal-coordinate treatment on another parent polyoxometalate, the hexamolybdate anion.[14]

IR and Raman frequencies of the studied compounds are given throughout the preparation section. The frequencies subjected to discussion are listed in Tables I and II, with the corresponding assignments.

(ii) Cation-Size Effect on the M–O_d Stretchings. As mentioned above, the alkaline-cation-size effect cannot be studied independently from the expected effects arising from the polarizing power and from the perturbation due to crystallization water molecules. The tetraalkylammonium cation series seems then more convenient for such a study. Indeed, all the R_4N^+ counterions exhibit a very low polarizing power, they are not

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Table I. Some Important Assignments in the Vibration Spectra of XMo$_{12}$ Anions according to the Counterion[a]

			Δν, cm^{-1}/activity/assignment						
no.	anion	cation	±0.25/R/ ν_s(Mo-O$_d$)	±1/R/ ν_{as}(Mo-O$_d$)	±0.5/IR/ ν_{as}(Mo-O$_d$)	±1/IR/ ν_{as}(X-O$_a$)	±1/IR/ ν_{as}(Mo-O$_b$-Mo)	±1.5/IR/ ν_{as}(Mo-O$_c$-Mo)	±1/R/ ν_s(Mo-O$_a$)
Ik	α-SiMo$_{12}$	TBA	967.5	941.5	945 940	899	868	795	246.5
Ie	α-SiMo$_{12}$	Gua	978.5	964	957 949	900	865	790	249
Ia	α-SiMo$_{12}$	H	988	963.5	957	904	855	770	250.5
IIk	β-SiMo$_{12}$	TBA	970.5	943.5	945	895	857	800	245
IIIk	α-GeMo$_{12}$	TBA	967.5	940	939	812	873	778	247
IIIc	α-GeMo$_{12}$	Na	979.5	961.5	960	808	895	775	247.5
IIIa	α-GeMo$_{12}$	H	986	960	951	790	870	760	250
IVk	β-GeMo$_{12}$	TBA	970	942	945	812	875	773	246
Vl	α-PMo$_{12}$	THA	986	965.5	964 954	1062	878	803	247
Vk	α-PMo$_{12}$	TBA	986	971 964	965 955	1063	880	805	246
Vc	α-PMo$_{12}$	Na	995.5	979 966.5	962	1068	869	785	251.5
Va	α-PMo$_{12}$	H	995.5	980 972	975 963	1067	870	810 785	251
VIk	β-PMo$_{12}$	TBA	988	968	965 953	1056	882	804	244
VIIk	α-AsMo$_{12}$	TBA	986	961	965	895	855	790	247
VIIb	α-AsMo$_{12}$	Li	993.5	976	969 963	906 895	846	773	250
VIIIk	β-AsMo$_{12}$	TBA	987	965	965	890		788	244.5

[a] Δν = accuracy, R = Raman, IR = infrared.

Table II. Some Important Assignments in the Vibration Spectra of XW$_{12}$ Anions according to the Counterion[a]

			Δν, cm^{-1}/activity/assignment						
no.	anion	cation	±0.25/R/ ν_s(W-O$_d$)	±1/R/ ν_{as}(W-O$_d$)	±0.5/IR/ ν_{as}(W-O$_d$)	±1/IR/ ν_{as}(X-O$_a$)	±1/IR/ ν_{as}(W-O$_b$-W)	±1.5/IR/ ν_{as}(W-O$_c$-W)	±1/R/ ν_s(W-O$_a$)
IXk	α-BW$_{12}$	TBA	971	951	950	900		817	210
IXd	α-BW$_{12}$	K	981.5	961.5	960	910		807	212
Xk	α-SiW$_{12}$	TBA	987	966	967	920	883	797	218.5
Xh	α-SiW$_{12}$	TMA	992	971.5	975	920	882	790	221
Xf	α-SiW$_{12}$	Ba	999	984 969	981	925	892 878	780	223
Xd	α-SiW$_{12}$	K	995	984.5 966	980	925	894 878	780	220.5
Xa	α-SiW$_{12}$	H	1000	975	981	928	880	785	222
XIl	β-SiW$_{12}$	THA	988.5	969	969	914	868	810 790	211
XIk	β-SiW$_{12}$	TBA	988.5	968.5	969	914	870	809 793	210
XIj	β-SiW$_{12}$	TPA	989	969	970	913	870	800	210
XIi	β-SiW$_{12}$	TEA	989.5	971	973	915	870	793	211
XIh	β-SiW$_{12}$	TMA	991.5	974	976	915	870	790	209
XIg	β-SiW$_{12}$	NH$_4$	995	974	979	915	855	785	213
XIe	β-SiW$_{12}$	Gua	994	978	980	917	865	790	211
XId	β-SiW$_{12}$	K	999	983	984	917	865	791	214.5
XIa	β-SiW$_{12}$	H	999	983	980	920		790	213.5
XIIk	α-GeW$_{12}$	TBA	986	964	965	830	895 885	780	221
XIId	α-GeW$_{12}$	K	991.5	971	979	823	880	769	221.5
XIIa	α-GeW$_{12}$	H	1001	974.5	980	818	903 883	760	226
XIIIk	β-GeW$_{12}$	TBA	986.5	964.5	967	830	890 875	780	212
XIIId	β-GeW$_{12}$	K	999	982	980	828	895	775	217
XIIIa	β-GeW$_{12}$	H	999	979	980	825	895	775	218
XIVk	α-PW$_{12}$	TBA	1003.5	993 986	987 976	1080	895	810	215.5
XIVc	α-PW$_{12}$	Na	1012.5	992.5	995 982	1081	900	805	218
XIVa	α-PW$_{12}$	H	1007	992 983.5	990 982	1080	890	810	217.5
XVk	α-AsW$_{12}$	TBA	1000.5	984	983	912	873	793	220.5
XVc	α-AsW$_{12}$	Na	1004	989	987	911	872	781	220

[a] Δν = accuracy, R = Raman, IR = infrared.

Table III. Interatomic Distances between Next Anions in the Crystal Lattice of XM_{12} Compounds of Known Structure

anion	cation	n H_2O	R^a	Z^b	V^c	r^d	X-X^e	O_d-O_d^{f}	O_d-O_b^{f}	O_d-O_c^{f}	ref
α-SiW_{12}	K	17	0.102	3	4009	5.20	10.459	3.138	3.392	3.505	16
α-SiW_{12}	Ba	16	0.13	4	4811	5.22	9.729	2.913	2.724	3.727	17
α-SiW_{12}	TMA	0	0.057	2	2724	5.22	12.147	3.273	4.010	3.301	18
β-SiW_{12}	K	9	0.138	4	4157	5.22	10.180	2.874	4.057	2.920	19
β-SiW_{12}	TBA	0	0.106	4	9988	5.13	13.638	6.068	7.012	6.630	18
α-PW_{12}	H	6	0.031	2	1794	5.23	10.52	3.344	3.407	3.213	20
α-$SiMo_{12}$	H	13	0.049	2	2116	5.17	9.638	2.914	2.940	3.677	21
α-$SiMo_{12}$	Gua	1	0.064	2	2168	5.17	9.738	2.989	2.998	2.959	22
α-$GeMo_{12}$	Na	8	0.029	2	1928	5.18	9.755	2.818	2.889	2.895	23
α-PMo_{12}	H	29-31	0.047	4	6332	5.22	10.09	3.171	4.336	3.016	24

^{a} R = reliability factor. ^{b} Z = number of molecules in the cell. ^{c} V = cell volume (Å³). ^{d} r = radius of the anionic sphere (Å). ^{e} X-X = shortest distance between two next atoms (Å). ^{f} O_d-O_d, O_d-O_b, and O_d-O_c = shortest distances between the O_d atoms of one anion and the O_d, O_b, and O_c atoms of the next anions (Å).

hydrogen-bond donors, and they generally give water-free compounds with polyanions.[15]

So, according to the zero-order approximation used until now, all the R_4N^+ salts of the same polyanion were expected to give the same spectra (except for the bands characteristic of the cation).

This is not observed, and moreover, the M–O_d stretching frequencies are considerably lower for the TBA or THA salts than for all the other ones (Tables I and II).

This experimental fact, inconsistent with the hypothesis pointed out above, induced us to reconsider this approximation, likely too crude: we had to envisage the anion–anion interactions (abbreviated (A–A) interactions).

It was then important to consider the structural determinations of this kind of compounds in order to know, according to the counterion, the arrangement of the anions in the cell, the distances between the anions, and the eventual (A–A) interactions.

Structural determinations of particular importance for our purpose are listed in Table III. Each anion can be inscribed into a sphere of center X and radius ~5.2 Å (radius = mean of the 12 X–O_d distances). The distance between two next X atoms is, in most cases, about twice the radius of the sphere and can even be lower when the counterion is relatively small. Then, with the anionic spheres being in contact or even interpenetrating, (A–A) interactions can be considered, the nature of which will be tentatively defined below. On the other hand, long X–X distances are in favor of weaker (A–A) interactions (e.g., β-SiW_{12}TBA).

When only the space group and the number of formula units in the cell are known, the volume of the cell also gives interesting information about the eventual (A–A) interactions. The high value for β-SiW_{12}TBA is consistent with weak interactions. In contrast, all the other values show that stronger (A–A) interactions had to be expected.

These (A–A) interactions may arise from the repelling of negative charge densities carried by the external oxygen atoms.

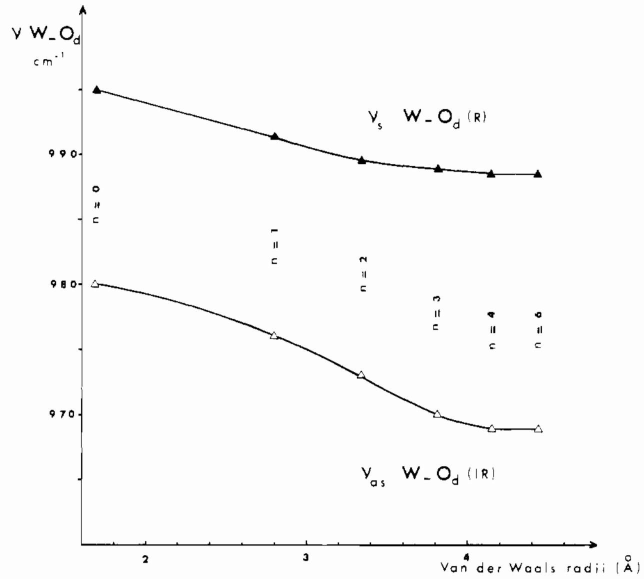

Figure 2. Plot of the ν(W–O_d) frequencies of β-SiW_{12} vs. the van der Waals radii of tetraalkylammonium cations $(C_nH_{2n+1})_4N^+$ (the limit case of ammonium counterion, namely n = 0, is included in the series).

In order to evaluate these interactions, we have then calculated the distances between the O_d, O_b, and O_c atoms belonging to adjacent polyanions (Table III; only the shortest distances are reported).[25]

From the information gathered in Table III, it can be seen that these large anions generally impose a relatively close packing, which leaves enough room for small or intermediate-size cations and for crystallization water molecules. This rule is no longer obeyed with the TBA cation, which is by far larger[26] than the other ones listed in Table III and plays the most important role in the packing: the anions are compelled to stay far apart.

From this structural information, it is clear that the cation size determines the (A–A) interactions: the larger the cation, the longer the interanion O–O distances and, consequently, through the electrostatic repelling hypothesis formulated above, the weaker the (A–A) interactions.

Then the correlation between the cation size and the M–O_d stretching frequencies has been investigated, giving special emphasis to the R_4N^+ series since, in this case, only the (A–A)

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(15) A few R_4N^+ salts retain one or two water molecules of zeolitic nature, according to the TG analysis; these water molecules have no influence on the vibrational spectra.

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(25) The values are not known with the same precision. Therefore, they have to be considered with some prudence in the case of compounds for which the reliability factor is rather poor: some values calculated for α-SiW_{12}Ba (R = 0.13) and β-SiW_{12}K (R = 0.138) are particularly low and could be questioned.

(26) In the absence of exhaustive crystallographic data about the size of R_4N^+ cations, we shall use the van der Waals radii, recently evaluated: Krumgalz, B. S. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 437.

interactions are expected to be responsible for the frequency shifts. Let us note that the M–O_d stretching modes are more suitable than the other M–O stretching modes for such a correlation because they are almost pure modes and they give rise to relatively sharp bands, which allow good precision in the determination of the frequencies.

From the results reported in Tables I and II and in Figure 2, it appears that each ν(M–O_d) mode is a decreasing function of the cation size.[26] The curve of Figure 2 tends toward a limit for high values of van der Waals radii, which agrees with the electrostatic repelling hypothesis. This limit corresponds to the absence of (A–A) interactions, i.e., to the case for which the zero-order approximation strictly applies. In the case of β-SiW_{12}, the lowest limit is already reached with the TBA cation (4 TBA/anion): the still larger THA cation introduces no supplementary lowering of the ν(W–O_d) frequencies. It is clear that a rather long interanionic distance (greater than 6 Å) is required for neglecting the (A–A) interactions. The term just before the limit, namely the TPA cation, for which, in the absence of crystallographic data, we expect interanionic distances in the range 4–5 Å, must involve however (A–A) interactions according to the frequency shifts: the vibrational techniques appear here to be powerful enough to detect such tiny interactions.

In order to check whether the stretching frequencies of the TBA salts were also the lowest ones for anions carrying only three negative charges (3 TBA/anion), we have prepared α-PMo_{12}THA already reported:[27] the ν(Mo–O_d) frequencies of this compound are the same as those of α-PMo_{12}TBA (Table I). It is then reasonable to assume that the (A–A) interactions can be neglected for all the TBA salts, for which the isolated anion model can be applied: the ν(M–O_d) frequencies of the TBA compounds can be considered as the true ν(M–O_d) stretching frequencies of the isolated anion.

With the other salts involving smaller counterions, a shift with respect to the TBA salts is observed toward the high frequencies. This shift can be correlated with the (A–A) interactions, through the interanionic O–O distances listed in Table III: the higher the shift, the shorter the distances, i.e., the stronger the interaction. Nonnegligible electrostatic forces occurring between the external oxygens of the adjacent anions, the expression of the potential energy includes, in addition to the terms corresponding to the stretching of the M–O_d oscillators, some additional terms of the form qq'/d, q being the charge carried by the O_d atoms of one anion, q' the charge carried by the external oxygens (O_d, O_b, or O_c) of its next neighbors, and d the distance between the concerned oxygens. These additional terms are all positive: thus, because of this perturbation, the potential energy is increased and, as a consequence, the corresponding frequency as well.

Unfortunately, we do not know the repartition of charges on the external oxygens of the polyanions. Our hope to get it from the observed frequency shifts vanishes since there are three unknowns (the charges on O_d, O_b, and O_c atoms) and only one equation (the approximate expression of the potential energy). If only the O_d's were acting in these electrostatic interactions, we could give a rough evaluation of their density of charge. But the interactions due to the O_b's and O_c's can never be neglected, according to the computed distances listed in Table III. Hence, we are able to give only a qualitative explanation to the frequency shifts observed.

(iii) Cation-Size Effect on the Other Stretching Vibrations. We have pointed out above that the (A–A) interactions are negligible in the case of solid TBA compounds, which can be considered as the best models we can propose for isolated anions and will be used below as references.

Let us now consider the IR bands in the 890–850- and 800–760-cm^{-1} spectral regions. These bands, respectively named I and II, are usually described as ν_{as}(M–O_b–M) ("inter" bridge stretchings) and ν_{as}(M–O_c–M) ("intra" bridge stretchings), the latter being particularly strong and broad. This description is only approximate: these vibrations are not pure and cannot be free from bending character, as shown clearly by the experimental results.

For all the compounds, except the TBA ones, electrostatic anion–anion interactions (effect A) are expected. This effect leads to an increase in the stretching frequencies with respect to the reference spectra (effect As). Because of the complex nature of the bridge stretching vibrations, we have to consider how the anion–anion interactions act on the bending vibrations (effect Ab). By comparison with the results obtained from a normal-coordinate analysis of the hexamolybdate anion,[14] we could assign band II to the ν_{as}(M–O_c–M) stretching with some character of O_d–M–O_c bending and the strong 385–370-cm^{-1} IR band to a vibration with a predominant O_d–M–O_c bending character. Now the frequency of the later band is significantly higher for the TBA complexes than for the other ones. We could then assume that effect A leads to a decrease in the bending vibration frequencies. What now happens with a vibration that presents both stretching and bending characters and that is sensitive to effect A? Its frequency will be so much higher as the bending character will be weaker (competition between the two opposite effects As and Ab).

Moreover, perturbations due to water molecules and/or anion–cation interactions (effect B) lead to a decrease in the frequencies of bands I and II and can strengthen the eventual effect Ab.

In the competition of the opposite effects, on the one hand, As, and, on the other hand, Ab and B, the decreasing effect is often stronger than the increasing one, particularly for band II. For instance, ν_{as}(M–O_c–M) stretchings are respectively observed at 795, 790, and 770 cm^{-1} for α-$SiMo_{12}$TBA, α-$SiMo_{12}$Gua, and α-$SiMo_{12}$H. A relatively strong effect A is expected for α-$SiMo_{12}$Gua from crystallographic data (Table III): the frequency is however lower than that of the TBA reference compound because of the effect Ab that is strengthened by the effect B (the distances N···O between the Gua counterion and the anion are consistent with NH···O hydrogen bonds[28]). A weaker effect A (Table III) and a stronger effect B make the frequency of α-$SiMo_{12}$H much lower. Similar considerations can be made for the other compounds.

It appears that the decreasing effect is always predominant on band II. Such a general rule is not always obeyed for band I: the increasing effect (As) is either stronger (e.g., α-SiW_{12} compounds) or weaker (e.g., α-$SiMo_{12}$ compounds) than the decreasing one (Ab + B).

The Raman ν_s(M–O_c–M) band will not be considered in the discussion, because its broadness and low intensity make any correlation insignificant.

Except for X = P, the frequency of the vibration assigned as ν_{as}(X–O_a) depends on the counterion. This is consistent with a mixed vibration, with a strong character of M–O_b–M stretch. This band has often a dissymmetric shape and is rather broad, which is also in agreement with the assumption of a mixed vibration. The different components of this band cannot be split by lowering the temperature. We already assumed that the 917-cm^{-1} IR band of β-SiW_{12}K presented some "inter" bridge stretching character.[13]

The strong Raman band usually described as "ν_s(M–O_a)" (Tables I and II) depends as well on the counterion, but to a less extent. This is also consistent with a mixed vibration,

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with an important bridge stretching character, as it has been proved for the "ν_s(Mo–central oxygen)" mode in the hexamolybdate anion.[14]

Conclusion

In this study of a great number of polyoxo compounds related to the Keggin structure, we have demonstrated that, in most cases, anion–anion interactions of electrostatic type are responsible for a strong increase in the stretching frequencies. These interactions have been correlated with the cation size, since the higher the M–O_d stretching frequencies, the smaller the cation. These interactions vanish when the counterion is large enough to keep the polyanions far apart (e.g., the TBA counterion). A minimal distance of about 6 Å between the external oxygens of adjacent polyanions seems required for neglecting anion–anion interactions.

The solid TBA compounds can be proposed as good models for isolated anions in the crystal lattice and can be used as references. The vibrational techniques are proved to be efficient for detecting and interpreting slight effects difficult to study with crystallographic techniques.

Further work dealing with solvent effect on these compounds is now in progress.

Acknowledgment. The authors wish to thank Prof. J. P. Perchard for helpful discussions concerning electrostatic interactions.

Note Added in Proof. A recent paper (Fuchs, J.; Thiele, A.; Palm, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 789) reports preliminary results about the structure of α-PW_{12}TBA ($V = 8526.3$ Å^3, $Z = 4$): these results agree with our conclusions (see text and Table III).

Registry No. Ia, 12027-12-2; Ie, 75329-24-7; Ik, 59138-97-5; IIIa, 12411-35-7; IIIc, 67954-33-0; IIIk, 81205-59-6; Va, 12026-57-2; Vc, 55624-58-3; Vk, 53749-36-3; Vl, 3844-82-0; VIIb, 83844-89-7; VIIk, 81158-05-6; IXd, 11078-54-9; IXk, 83844-83-1; Xa, 12027-38-2; Xd, 12027-46-2; Xf, 12161-28-3; Xh, 77214-65-4; Xk, 51542-99-5; XIe, 83861-67-0; XIg, 77981-80-7; XIi, 83844-84-2; XIj, 83844-85-3; XIl, 83844-86-4; XIIa, 12207-33-9; XIId, 83844-90-0; XIIk, 83844-87-5; XIVa, 1343-93-7; XIVd, 12026-98-1; XIVk, 53749-37-4; XVc, 78143-04-1; XVk, 83844-88-6.

Supplementary Material Available: Discussion of thermogravimetry experiments and tables of TG results (3 pages). Ordering information is given on any current masthead page.

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Photoelectron Spectroscopy of f-Element Organometallic Complexes. 3. Chloro, Bromo, Methoxy, and Methyl Complexes of Triindenylthorium(IV) and -uranium(IV)

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Received February 5, 1982

This paper presents a study of photoelectron spectra of a series of triindenylactinide(IV) complexes containing various σ-bonded ligands. Studies were performed with both He I and He II ionizing sources. The first data on details of the valence electronic structure have been obtained. It is found that the bonding of the ring ligand in indenyl complexes is similar to that found in corresponding cyclopentadienyl complexes even though there are indications of a greater 5f covalency in the former. Along the series of the studied complexes, differences have been found as far as the nature of the σ-bonded ligand is concerned. There is evidence, in $U(ind)_3CH_3$, of a tendency toward ionicity, which can account for the observed band shape associated with the $5f^{-1}$ ionization in its spectrum.

Introduction

Ultraviolet photoelectron (PE) spectroscopy has proven to be an important technique for studying the electronic structure of actinide complexes.[2] It has provided revelant information about perturbations due to actinide valence orbitals on the ligation environment. Various classes of actinide compounds including both organometallic[3,4] and classical coordination[5] complexes have thus far been studied. Complexes of the indenide ligand are of particular interest among actinide organometallics. Their coordination closely resembles that in corresponding cyclopentadienyl complexes even though variations due to the greater steric demand of the ligand and to the involvement in the bonding of electrons mainly localized on the six-membered ring of the indenide anions cannot be excluded a priori. In this paper we report on He I and He II excited PE spectra of the triindenylactinide complexes $An(C_9H_7)_3X$ ($An = Th, U$) containing various σ-bonded ligands ($X = Cl, Br, OCH_3, CH_3$). Motivation for the study is the almost unique possibility offered by PE spectroscopy utilizing variable photon energies of elucidating the energy ordering of valence molecular orbitals and their atomic compositions. This information, *directly* related to metal–ligand bonding, becomes particularly valuable as the most reliable rationale for he physicochemical properties of present complexes since only *indirect* insight on the bonding properties has thus far been obtained[6] generally from reactivity data.

Experimental Section

The complexes under study were prepared as described elsewhere.[7] They were purified by sublimation in vacuo. Sample manipulations were carried out in a glovebox under inert atmosphere.

Spectra were run on a commercial Perkin-Elmer PS 18 spectrometer modified for He II measurements by including a hollow-cathode discharge lamp giving a high yield of He II photons (Helectros Development). The ionization energy (IE) scale was calibrated by reference to peaks due to admixed inert gases and to He $1s^{-1}$ self-ionization. Qualitative evaluations of band areas were generally precluded by the complexity of the spectral bands. Thus, intensity arguments were used in He I vs. He II comparison only when variations of peak height are clear and unambiguous.

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