

Hydrothermal Syntheses: A Route to the Stepwise Condensation of Reduced Keggin Polyanions. From Reduced β -[H_mSiMo₁₂O₄₀]ⁿ⁻ Monomers to Bicapped Dimerized [Si₂Mo₂₈O₈₄(H₂O)₂]⁶⁻ Anions

Anne Dolbecq, Emmanuel Cadot, Dirk Eisner, and Francis Sécheresse*

Institut Lavoisier, IREM, UMR 8637, Université de Versailles Saint-Quentin, 45 Avenue des Etats-Unis, 78035 Versailles, France

Received April 16, 1999

The five reduced polyoxomolybdate anions [HSiMo₁₂O₄₀]⁴⁻ (HI_β), [H₂SiMo₁₂O₄₀]⁴⁻ (H₂II_β), [H₅SiMo₁₂O₄₀]³⁻ (H₅IV_β), [SiMo₁₄O₄₄]⁴⁻ (SiMo₁₄), and [Si₂Mo₂₈O₈₄(H₂O)₂]⁶⁻ (Si₂Mo₂₈) have been synthesized as tetramethylammonium salts, by hydrothermal reactions, and characterized by IR spectroscopy, redox titrations (HI_β, H₂II_β), and X-ray crystal structure analyses. Crystal data: (TMA)₄HI_β·1.5H₂O, monoclinic space group *P*2₁/*n*, *a* = 12.2487(3) Å, *b* = 39.9307(11) Å, *c* = 12.4761(3) Å, β = 116.542(1)°; (TMA)₄H₂II_β·2H₂O, monoclinic space group *P*2₁/*n*, *a* = 12.7930(2) Å, *b* = 21.6171(2) Å, *c* = 19.7222(2) Å, β = 96.017(1)°; (TMA)₃H₅IV_β·2H₂O, monoclinic space group *P*2₁/*n*, *a* = 12.7763(5) Å, *b* = 20.2277(8) Å, *c* = 20.9784(9) Å, β = 98.037(1)°; (TMA)₄SiMo₁₄, monoclinic space group *P*2₁/*n*, *a* = 12.0502(4) Å, *b* = 11.7500(4) Å, *c* = 19.8001(5) Å, β = 100.525(1)°; (TMA)₆Si₂Mo₂₈·2H₂O, monoclinic space group *P*2₁/*n*, *a* = 19.3591(2) Å, *b* = 13.1119(2) Å, *c* = 21.1265(2) Å, β = 101.124(1)°. HI_β, H₂II_β, and H₅IV_β are respectively one-, two-, and four-electron-reduced {SiMo₁₂O₄₀} anions with the β-Keggin type structure. SiMo₁₄ and Si₂Mo₂₈ are two novel anions containing α-Keggin cores; in SiMo₁₄ the Keggin core is capped by two {MoO₂} units while in Si₂Mo₂₈ two bicapped anions are linked through terminal oxo groups. A comparison of the molecular structures of the five anions shows the role of the protonation, the reduction, and the aggregation of capping {MoO₂} units on the structural features of the Keggin core. The condensation process is discussed in terms of Lewis-type interactions between reduced, highly charged basic polyanions and reactive {MoO₂}²⁺ units.

Introduction

The structural chemistry of phosphomolybdate and silicomolybdate anions has been extensively studied in recent years.¹ Polyoxometalates are of fundamental and practical interest, in particular for catalysis,² and despite their very old discovery, there is still a growing interest for the synthesis of new polyoxometalates and in particular reduced derivatives. However, whereas the reduction of polyoxometalates has been extensively studied in solution, either aqueous or nonaqueous, few crystallographic structures have been reported. Synthetic routes are now being developed, such as hydrothermal techniques, to obtain new reduced Keggin derivatives.³ We are currently interested in the synthesis of sulfur-rich polyoxomolybdates based on the {Mo^V₂S₂O₂} building block. The first member of this new family is the cyclic neutral [Mo₁₂S₁₂O₁₂(OH)₁₂(H₂O)₆] molecule.⁴ This molecule proved to be a convenient starting material as it regenerates straightforwardly the [Mo₂S₂O₂]²⁺ thioanion in acid solutions. The condensation

of the thioanion in the presence of an organic or inorganic structuring agent has thus afforded several new cyclic anions: [Mo₈S₈O₈(OH)₈(C₂O₄)₂]²⁻,⁵ [Mo₉S₈O₁₂(OH)₈(H₂O)₂]²⁻,⁶ [(HXO₄)₄-Mo₆S₆O₆(OH)₃]⁵⁻,⁷ and [(HXO₄)₂Mo₁₂S₁₂O₁₂(OH)₁₂(H₂O)₂]⁴⁻⁸ (X = P, As). In the course of our study, we have also explored the chemistry of the dinuclear thioanion under hydrothermal conditions, in the presence of phosphate or silicate anions. The variety of compounds based on the fully oxygenated analogue [Mo₂O₄]²⁺ cation was indicating that new oxothio compounds could be obtained in this way. However we have found that the {Mo₂S₂O₂} core was unstable under hydrothermal conditions and gave unexpected fully oxygenated Keggin-type compounds. We thus describe in this paper the hydrothermal syntheses and X-ray crystal structures of five mixed-valence Keggin-type heteropolymolybdates, crystallized as tetramethylammonium salts. Three are reduced derivatives of the well-known Keggin polyanion β-[SiMo₁₂O₄₀]⁴⁻, with different protonation and reduction states, [HSiMo^VMo^{VI}₁₁O₄₀]⁴⁻ (HI_β), [H₂SiMo^V₂Mo^{VI}₁₀O₄₀]⁴⁻ (H₂II_β), and [H₅SiMo^V₄Mo^{VI}₈O₄₀]³⁻ (H₅IV_β), and the other two, [SiMo^V₄Mo^{VI}₁₀O₄₄]⁴⁻ (SiMo₁₄) and [Si₂Mo^V₁₄Mo^{VI}₁₄O₈₄(H₂O)₂]⁶⁻ (Si₂Mo₂₈), have a higher nuclearity and have never been described so far. The formation of these five

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Table 1. Crystallographic Data

	(TMA) ₄ HI _β ·1.5H ₂ O	(TMA) ₄ H ₂ II _β ·2H ₂ O	(TMA) ₃ H ₅ IV _β ·3.5H ₂ O	(TMA) ₄ SiMo ₁₄	(TMA) ₆ Si ₂ Mo ₂₈ ·2H ₂ O
formula	C ₁₆ H ₅₂ Mo ₁₂ N ₄ O _{41.5} Si	C ₁₆ H ₅₄ Mo ₁₂ N ₄ O ₄₂ Si	C ₁₂ H ₄₈ Mo ₁₂ N ₃ O _{43.5} Si	C ₁₆ H ₄₈ Mo ₁₄ N ₄ O ₄₄ Si	C ₁₂ H ₄₀ Mo ₁₄ N ₃ O ₄₄ Si
fw	2145.3	2154.0	2109.9	2371.8	2301.7
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	12.2487(3)	12.7930(2)	12.7763(5)	12.0502(4)	19.3591(2)
<i>b</i> , Å	39.9307(11)	21.6171(2)	20.2277(8)	11.7500(4)	13.1119(2)
<i>c</i> , Å	12.4761(3)	19.7222(2)	20.9784(9)	19.8001(5)	21.1265(2)
β, deg	116.542(1)	96.017(1)	98.037(1)	100.525(1)	101.124(1)
<i>V</i> , Å ³	5458.9(2)	5424.1(1)	5368.3(4)	2756.3(2)	5261.9(1)
<i>Z</i>	4	4	4	2	4
ρ _{calc} , g cm ⁻³	2.609	2.638	2.611	2.858	2.905
μ, cm ⁻¹	27.81	28.00	28.28	31.95	33.42
<i>R</i> (<i>F</i> _o) ^a	0.068	0.051	0.050	0.071	0.054
<i>R</i> _w (<i>F</i> _o ²) ^b	0.140	0.123	0.124	0.185	0.121

^a $R = \sum |F_o| - |F_c| / (\sum |F_c|)$. ^b $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$ with $1/w = \sigma^2 F_o^2 + (aP)^2 + bP$ and $a = 0.0304$, $b = 117.04$ for HI_β; $a = 0.0510$, $b = 67.27$ for H₂II_β; $a = 0.0526$, $b = 89.70$ for H₅IV_β; $a = 0.1098$, $b = 10.66$ for SiMo₁₄; $a = 0.0520$, $b = 74.30$ for Si₂Mo₂₈.

anions depends on the heating temperature of the hydrothermal syntheses and on the pH of the reaction solution. Three of them (H₅IV_β, SiMo₁₄, Si₂Mo₂₈) were first obtained starting from the oxothio precursor [Mo₁₂S₁₂O₁₂(OH)₁₂(H₂O)₆], and the other two (H₂II_β, HI_β) were prepared from a mixture of Mo and Na₂MoO₄, as a source of molybdenum.

Experimental Section

Synthesis. The hydrothermal syntheses were carried out in poly-(tetrafluoroethylene) lined stainless steel containers under autogenous pressure. Unless otherwise specified, the 23 mL vessel was filled to approximately 13% volume capacity (*V*_i = 3 mL). All reactants were stirred briefly before heating. The samples were heated for 36 h either at 150 °C or at 180 °C and cooled to room temperature over a period of 10 h. The pH of the reaction mixture was measured before (pH_i) and after the reaction (pH_f). The products were isolated by decantation and ethanol washing.

The syntheses of H₅IV_β, SiMo₁₄, and Si₂Mo₂₈ were carried out with [Mo₁₂S₁₂O₁₂(OH)₁₂(H₂O)₆]^{14,6} as a precursor, Na₂SiO₃, HCl, tetramethylammonium hydroxide (TMAOH), and H₂O in the mole ratio 1:2:100: *n*:5000, with *n* as a variable parameter to adjust the initial pH. The heteropolyoxomolybdate H₅IV_β was obtained for pH_i = 5.0 (pH_f = 1.6) and a heating temperature of 180 °C. Anion SiMo₁₄ was synthesized at 150 °C, for pH_i = 4.0 (pH_f = 1.3), while the dimerized anion Si₂Mo₂₈ was isolated at 180 °C, for a starting pH 2.0 (pH_f = 1.3).

The heteropolyoxomolybdates HI_β, H₂II_β, and HII_β were synthesized from a mixture of Mo (325 mesh), Na₂MoO₄·2H₂O, Na₂SiO₃, HCl, TMAOH, and H₂O in the mole ratio 1:5:1:30:*n*:2000, with *n* as a variable parameter to adjust the pH. The heating temperature was 180 °C. For pH_i = 6.0 (pH_f = 5.7), 60 mg of crystals of HII_β was isolated (yield 57%, based on Mo). Anal. Calcd (found) for [N(CH₃)₄]₅[HSiMo₁₂O₄₀]·6H₂O: C, 10.44 (10.65); N, 3.05 (3.19); Mo, 50.10 (50.21); Si, 1.22 (1.60). When pH_i ≤ 3.0 (pH_f ≤ 3.1), a mixture of H₂II_β and HI_β was obtained. When the 23 mL reaction vessel was filled to approximately 40% volume capacity (*V*_i = 9 mL), SiMo₁₄ was the main product of the reaction.

Chemical analyses have been performed on samples containing HI_β, H₂II_β, and HII_β. The redox back-titration for the determination of the amount of Mo⁵⁺ ions is based on the oxidation of Mo⁵⁺ by Ce⁴⁺. The sample (about 50 mg) was dissolved in 20 mL of water and excess Ce⁴⁺ solution (0.05 M); the excess Ce⁴⁺ was titrated potentiometrically with Fe²⁺ (0.1 M).

Infrared spectra were recorded on an IRFT Magna 550 Nicolet spectrophotometer at 0.5 cm⁻¹ resolution, using the technique of pressed KBr pellets.

Magnetic Studies. The magnetic data were recorded on a 21.3 mg polycrystalline sample containing a mixture of HI_β and H₂II_β, synthesized at pH_i = 3, over the 4–300 K temperature region, at a magnetic field of 5000 G, using a Quantum Design SQUID magnetometer.

X-ray Crystallography. Intensity data collection was carried out at room temperature with a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector using the monochroma-

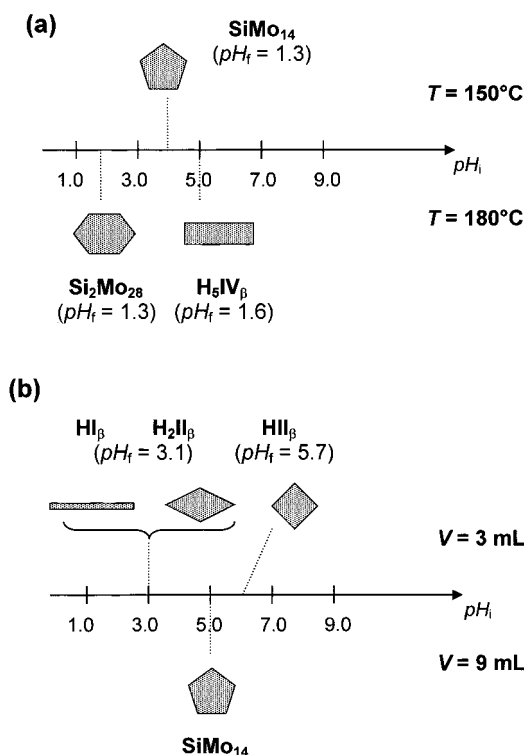


Figure 1. Synthesis conditions for the five polyanions: (a) with the [Mo₁₂S₁₂O₁₂(OH)₁₂(H₂O)₆] precursor; (b) with Mo and Na₂MoO₄ as starting materials.

tioned wavelength λ(Mo Kα) = 0.710 73 Å. An empirical absorption correction was applied using the SADABS program⁹ based on the method of Blessing.¹⁰ The structures were solved by direct methods and refined by full-matrix least-squares using the SHELX-TL package.¹¹ The disordered oxygen atoms of the polyanion SiMo₁₄, as well as the disordered carbon atoms on the tetramethylammonium cations in the five structures, were refined isotropically, the other atoms being refined anisotropically. Hydrogen atoms on the non-disordered carbon atoms were placed at fixed positions using the program HFIX. Crystallographic data are given in Table 1. Selected bond distances and angles are listed in Table 2. Additional crystallographic information is given in the Supporting Information.

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Table 2. Selected Bond Distances (Å)

	HII _β	H ₂ II _β	H ₅ IV _β	SiMo ₁₄	Si ₂ Mo ₂₈
Si—O _a	1.633(10)–1.645(10) [1.627] ^a	1.611(8)–1.643(8) [1.627]	1.621(9)–1.629(9) [1.626]	1.515(12)–1.720(12) [1.627]	1.623(10)–1.641(9) [1.630]
Mo—O _a	2.335(10)–2.403(10) [2.374]	2.355(8)–2.404(8) [2.374]	2.355(8)–2.417(8) [2.387]	2.282(13)–2.512(12) [2.412]	2.367(9)–2.437(9) [2.396]
Mo—O _b short	1.837(9)–1.991(11) [1.909]	1.828(8)–1.981(9) [1.887]	1.844(8)–2.030(7) [1.925]	1.777(9)–2.055(13) [1.914] ^b	1.807(10)–1.965(10) [1.891]
long ^c					2.016(9)–2.066(10) [2.040]
Mo—O _c short	1.870(10)–1.989(10) [1.929]	1.876(9)–2.005(9) [1.930]	1.885(8)–1.951(10) [1.921]	1.777(9)–2.055(13) [1.914] ^b	1.811(13)–1.992(12) [1.904]
long ^c	2.075(9)–2.099(9) [2.087]	2.009(8)–2.114(8) [2.069]	2.046(7)–2.105(8) [2.082]		2.097(10)–2.128(9) [2.108]
Mo—O capped {MoO ₂ }				2.039(11)–2.069(10) [2.059]	1.967(10)–2.072(9) [2.001]
Mo—O _d	1.658(9)–1.694(10) [1.677]	1.659(8)–1.680(8) [1.669]	1.661(8)–1.685(7) [1.670]	1.619(12)–1.668(8) [1.640]	1.644(10)–1.691(9) [1.675]
Mo—O _t capped {MoO ₂ }					
short				1.62(2)–1.80(2)	1.698(8)–1.732(10)
long					2.182(10)–2.197(11)
Mo···Mo edge-sharing octahedra					
short	3.330–3.424 [3.405]	3.300–3.515 [3.420]	3.401–3.602 [3.453]	3.467–3.680 [3.542] ^b	3.217–3.357 [3.322]
long ^d					3.536–3.576 [3.556]
Mo···Mo corner-sharing octahedra					
short	3.609–3.751 [3.672]	3.603–3.712 [3.645]	3.581–3.700 [3.635]	3.467–3.680 [3.542] ^b	3.668–3.677 [3.672]
long ^d					3.858–3.948 [3.900]
Mo···Mo capped {MoO ₂ } and Keggin core				3.250–3.303 [3.280]	3.176–3.245 [3.205]

^a Mean values are indicated between square brackets. ^b These values are equal because of the disorder of the polyanion. ^c Mo—O distances for O atoms bridging two Mo atoms of the Keggin core with two corresponding Mo—O distances longer than 2.0 Å. ^d Distances between the Mo centers of the tetragonal faces bearing the capped {MoO₂} units.

Results and Discussion

Synthesis and Characterization. The reaction conditions for the synthesis of the five compounds and their crystal shapes are summarized in Figure 1. The reaction of the oxothiomolybdate compound [Mo₁₂S₁₂O₁₂(OH)₁₂(H₂O)₆]⁴⁻ with hydrochloric acid, silicate anions, and tetramethylammonium hydroxide, under hydrothermal conditions, afforded three unexpected, fully oxygenated Keggin derivatives: [H₅SiMo₁₂O₄₀]³⁻ (H₅IV_β), [SiMo₁₄O₄₄]⁴⁻ (SiMo₁₄), and [Si₂Mo₂₈O₈₄(H₂O)₂]⁶⁻ (Si₂Mo₂₈) as tetramethylammonium salts. The variable parameters were the initial pH value, controlled by the addition of TMAOH to the starting mixture, and the heating temperature. The heteropolyoxomolybdate H₅IV_β is obtained as the main product, for starting pH between 4.0 and 7.0, with an optimum value at 5.0. The capped anion SiMo₁₄ has only been obtained at 150 °C, for initial pH values close to 4.0, while the dimerized anion Si₂Mo₂₈ is formed for initial pH between 2.0 and 4.0, at 180 °C. Considering the nature of the final products of the reaction, we can conclude that, under hydrothermal conditions, the [Mo₁₂S₁₂O₁₂(OH)₁₂(H₂O)₆] precursor has been partially oxidized and subsequently decomposed. We then tried to prepare the mixed-valence anions by a more rational route, with molybdenum powder and sodium molybdate as precursors. It is indeed well-known that, under hydrothermal conditions, metallic molybdenum reduces Mo^{VI} atoms.¹³ The only variable param-

eters were the initial pH value and the total volume of reaction solution. The reaction with Mo metal afforded the heteropolyanions HII_β, in relatively good yield (57%, based on Mo) as a pure material and, for low pH, HII_β, mixed with H₂II_β. SiMo₁₄ can also be prepared in this way, for high volumes of solution, but H₅IV_β and Si₂Mo₂₈ were only obtained with the oxothio precursor. All five compounds are isolated as air-stable, dark blue, water-soluble crystals. The dark blue color is due to intervalence charge transfer transitions and is characteristic of “molybdenum blue” species,¹² which means that the silicomolybdate anions are mixed-valence compounds with Mo^V and Mo^{VI} atoms. It should be noted that the compounds prepared with the oxothio precursor are obtained in very low yield, dark blue crystals being mixed with the main product, which is an unidentified greenish powder, so that it was impossible to perform analytical measurements on these samples. The synthesis of H₅IV_β, SiMo₁₄, and Si₂Mo₂₈ is, however, perfectly reproducible, and these compounds have been characterized by single-crystal X-ray diffraction studies and IR spectroscopy measurements. On the other hand, the yields of the syntheses with Mo and Na₂MoO₄ as starting materials were high enough to allow analytical measurements. Chemical analyses have been performed on HII_β, HII_β, and H₂II_β, and elemental analysis is available for HII_β. The five compounds are easily distinguishable by the morphology of their crystals: the crystals shapes are respectively needles (HII_β), diamond shape platelets (H₂II_β), parallelepipeds, up to 1 mm long and often hollow (H₅IV), thick pentagonal platelets (SiMo₁₄), and hexagonal platelets (Si₂Mo₂₈).

Molecular Structures of the One-, Two-, and Four-Electron-Reduced β-12-Molybdosilicate Anions

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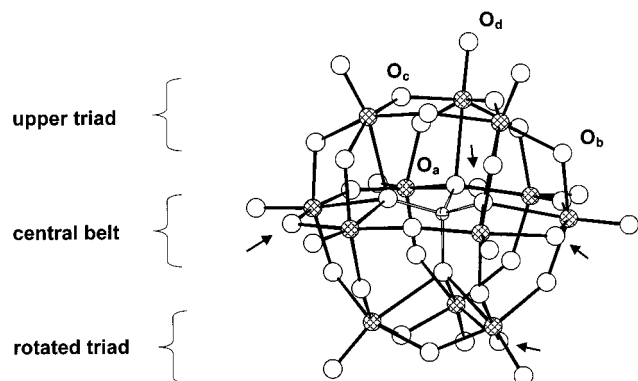


Figure 2. Ball-and-stick representation of the β -Keggin type anion $[\text{H}_5\text{SiMo}_{12}\text{O}_{40}]^{3-}$ ($\text{H}_5\text{IV}_\beta$): Mo atoms, crosshatched spheres; Si atom, white crossed spheres; O atoms, open spheres; protonated O atoms are marked with an arrow.

$[\text{HSiMo}_{12}\text{O}_{40}]^{4-}$ (HI_β), $[\text{H}_2\text{SiMo}_{12}\text{O}_{40}]^{4-}$ ($\text{H}_2\text{II}_\beta$), and $[\text{H}_5\text{SiMo}_{12}\text{O}_{40}]^{3-}$ ($\text{H}_5\text{IV}_\beta$). The anions HI_β , $\text{H}_2\text{II}_\beta$, and $\text{H}_5\text{IV}_\beta$ have the same overall molecular structure, namely, the β -Keggin type structure, represented in Figure 2. All three anions have no crystallographically imposed symmetry. The molybdenum atoms have a distorted octahedral coordination: they form Mo_3O_{13} units by sharing edges via $\text{Mo}-\text{O}_c-\text{Mo}$ connections with two other octahedra, the central oxygen atom (O_a) being bonded to the silicon atom. The four Mo_3O_{13} units are connected to each other by vertices, the bridging oxygen atoms between two adjacent Mo_3O_{13} units being labeled O_b . A terminal oxygen atom (O_d) completes the coordination sphere of the Mo centers. The β -Keggin type structure derives from the α -Keggin by a rotation of 60° of one of the Mo_3O_{13} units as shown in Figure 2. The three anions differ only by their reduction states and the number of protons attached to the oxygen atoms of the anion. Redox titrations have shown that HI_β and $\text{H}_2\text{II}_\beta$ were respectively one- and two-electron-reduced anions; this measurement was not possible for $\text{H}_5\text{IV}_\beta$ (see above). The oxidation state assignments for HI_β and $\text{H}_2\text{II}_\beta$ are consistent with the magnetic susceptibility studies. HI_β is expected to have a paramagnetic behavior while $\text{H}_2\text{II}_\beta$ is diamagnetic. The magnetic measurements were performed on a sample obtained at $\text{pH}_i = 3$, containing approximately 50% of HI_β and 50% of $\text{H}_2\text{II}_\beta$ (Figure 1). The temperature-dependent magnetic susceptibility data have been fitted with a Curie–Weiss law in the high-temperature domain (100–300 K), and the Curie constant $C = 0.145 \text{ emu K mol}^{-1} \text{ Oe}^{-1}$ has been determined, consistent with the presence of one-half unpaired electron per heteropolyanion. The charge of the anion, deduced from the number of tetramethylammonium cations, together with an examination of the Mo–O bond lengths and a calculation of bond valence sums,¹⁴ has allowed us to evaluate the number of protons and to localize them. In the structure of HI_β (respectively $\text{H}_2\text{II}_\beta$), one (two) O_c atoms, in the central belt, have low calculated bond numbers, 1.23 (1.15, 1.44) and are thus assumed to be protonated. The $\text{Mo}-\text{O}_c-\text{Mo}$ angles, 113.7° (112.8° , 115.6°), for these oxygen atoms are also quite a bit smaller than the average $\text{Mo}-\text{O}_c-\text{Mo}$ angles for nonprotonated anions (120.5°).¹⁵ The detailed formulas $[\text{HSiMo}^{\text{V}}\text{Mo}^{\text{VI}}_{11}\text{O}_{40}]^{4-}$ (HI_β) and $[\text{H}_2\text{SiMo}^{\text{V}}\text{Mo}^{\text{VI}}_{10}\text{O}_{40}]^{4-}$ ($\text{H}_2\text{II}_\beta$) derive immediately from these results. In the structure of $\text{H}_5\text{IV}_\beta$ (Figure 2), four sets of $\text{Mo}-\text{O}_c$ bond lengths [2.046–(7)–2.105(8) Å], three in the central belt and one in the tilted

Mo_3O_{13} unit, among edge-sharing octahedra, are significantly longer than the average $\text{Mo}-\text{O}_c$ bond length (1.93 Å) in the nonreduced structure¹⁵ and indicate that these bridging oxygen atoms are protonated, as also confirmed by the calculated bond numbers 1.18, 1.22, 1.28, and 1.31 valence units while for the other oxygen atoms they are in the range 1.80–2.21 valence units. The mean $\text{Mo}-\text{O}_c-\text{Mo}$ angle (115.3°) of these bonds is also quite a bit smaller than the averaged $\text{Mo}-\text{O}_c-\text{Mo}$ angle for nonprotonated anions (120.5°).¹⁵ A similar localization of the protons on the doubly bridging oxygen atom O_c (Figure 2) was proposed by Müller et al. for the four-electron-reduced β - $[\text{H}_4\text{AsMo}_{12}\text{O}_{40}]^{3-}$ anion.¹⁶ As only three tetramethylammonium cations have been located in the structure, the charge of the anion is assumed to be 3 and the detailed formula $[\text{H}_4\text{SiMo}^{\text{V}}\text{Mo}^{\text{VI}}_9\text{O}_{40}]^{3-}$ could be proposed. However, electrochemical studies¹⁷ on β - $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ have shown that, in this pH range ($\text{pH}_f = 1.6$), the first reduction steps correspond to three successive bielectronic transfers and the three-electron-reduced compound disproportionates via protonation into the four-electron-reduced species and the oxidized form. A four-electron-reduced species can thus be postulated. In addition, the reduced Keggin anions isolated in the solid state from acid solutions, described in the literature, are either two-electron-reduced anions, such as α - $[\text{HPMo}_{12}\text{O}_{40}]^{4-}$,¹⁸ α - $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{8-}$,¹⁹ and α - $[\text{H}_2\text{AsMo}_{12}\text{O}_{40}]^{3-}$,¹⁶ or four-electron-reduced species, as for β - $[\text{H}_x\text{PMo}_{12}\text{O}_{40}]^{7-x}$ ²⁰ and β - $[\text{H}_4\text{AsMo}_{12}\text{O}_{40}]^{3-}$.¹⁶ The structures of the two latter compounds are highly similar to the structure of $\text{H}_5\text{IV}_\beta$. In agreement with the charge of the anion, five protons are necessarily present. Four protons have been located by bond valence sum calculations; the additional H^+ is assumed to be disordered over the polyanion. The presence of five protons is also in agreement with the acidobasic properties of this anion. Indeed, β - $[\text{SiMo}_{12}\text{O}_{40}]^{8-}$ (IV_β) has eight acidities:¹⁷ two of them are strong, and the pK_a values of the other five have been determined experimentally to be 2.8, 3.8, 7.1, 9.5, and 11.5. As observed for β - $[\text{H}_x\text{PMo}_{12}\text{O}_{40}]^{7-x}$,²⁰ the net effect of the reduction is the expansion of the $\text{Mo}\cdots\text{Mo}$ distances between edge-sharing octahedra (Table 2) while the $\text{Mo}\cdots\text{Mo}$ separations between corner-sharing octahedra are shortened. We have obtained reduced β -Keggin anions with low reduction states (I_β , II_β) instead of the expected α isomers. This is quite surprising since it is commonly admitted that, in aqueous solution, at room temperature, the α isomer is the thermodynamically stable isomer, the β -isomer being known to be thermodynamically stable only from the fourth electron reduction state.^{12a} Thus hydrothermal conditions proved here to be efficient for the preparation of species that could not be formed by traditional synthesis routes.

Structure of the Heteropolyanion $[\text{SiMo}_{14}\text{O}_{44}]^{4-}$ (SiMo_{14}). This anion (Figure 3) can be described as an α -Keggin framework capped on two oppositely disposed tetragonal faces by $\{\text{Mo}^{\text{VI}}\text{O}_2\}$ subunits. The anion is disordered over two positions because of its location on a center of inversion, incompatible with the tetrahedral symmetry of the α -Keggin unit. This disorder is evidenced by the presence of eight oxygen atoms surrounding the central silicon atom, at the vertices of a

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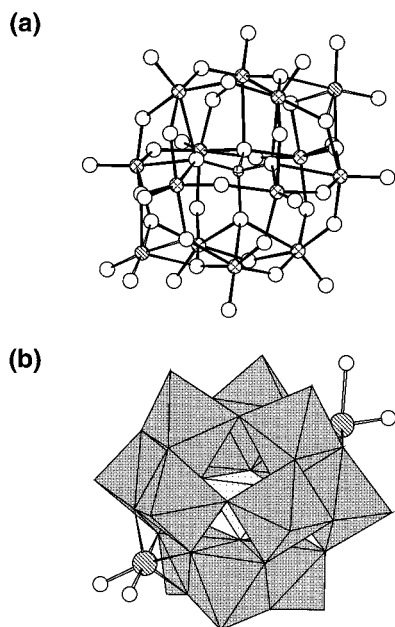


Figure 3. (a) Ball-and-stick representation of $[\text{SiMo}_{14}\text{O}_{44}]^{4-}$ (SiMo_{14}): Mo atoms of the capped $\{\text{MoO}_2\}$ fragments, hatched spheres. For clarity, only one-half of the disordered oxygen atoms are drawn. (b) Polyhedral representation.

cube, with half-occupancies, and it is also enhanced by the unusually large and elongated thermal ellipsoids of the other bridging oxygen atoms of the framework. This type of disorder has already been encountered a few times^{3b,18,21} and was first described by Evans and Pope.²² The terminal oxygen atoms of the capped $\{\text{MoO}_2\}$ units are also disordered over two half-occupied positions. The molybdenum atoms of these capped units have a highly distorted octahedral coordination with two short Mo–O_t bonds [1.62(2)–1.80(2) Å] and four remaining longer Mo–O bridging bonds [2.039(11)–2.073(10) Å] which complete the octahedral environment. Assuming that none of the bridging oxygen atoms is protonated, the detailed formula of the anion is $[\text{SiMo}^{\text{V}}_4\text{Mo}^{\text{VI}}_{10}\text{O}_{44}]^{4-}$. As the anion is disordered, the other geometrical features will be more favorably discussed in the structure of $\text{Si}_2\text{Mo}_{28}$. The aggregation of capping units to a reduced Keggin polyanion can be described as a Lewis-type interaction between the nonprotonated four-electron-reduced $[\text{SiMo}^{\text{V}}_4\text{Mo}^{\text{VI}}_8\text{O}_{40}]^{8-}$ species, acting as a base, and the $\{\text{Mo}^{\text{VI}}\text{O}_2\}^{2+}$ Lewis acid. This result shows that, depending on the synthesis conditions, the most basic oxygen atoms either protonate as observed for $\text{H}_5\text{IV}_\beta$ or react with an electrophilic molecule in solution.²³ This property is nicely used by Müller et al.²⁴ to grow large molecular systems. There have been a few bicapped α -Keggin derivatives described in the literature. The capping units are $\{\text{VO}\}$ units, as in $[\text{PMo}_{12}\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_2]^{5-}$,²⁵ $[\text{H}_4\text{PV}_{12}\text{O}_{40}(\text{V}^{\text{V}}\text{O})_2]^{5-}$,²⁶ and $[\text{AsV}_{12}\text{O}_{40}(\text{V}^{\text{V}}\text{O})_2]^{9-}$,²⁷ $\{\text{As}^{\text{III}}\}$

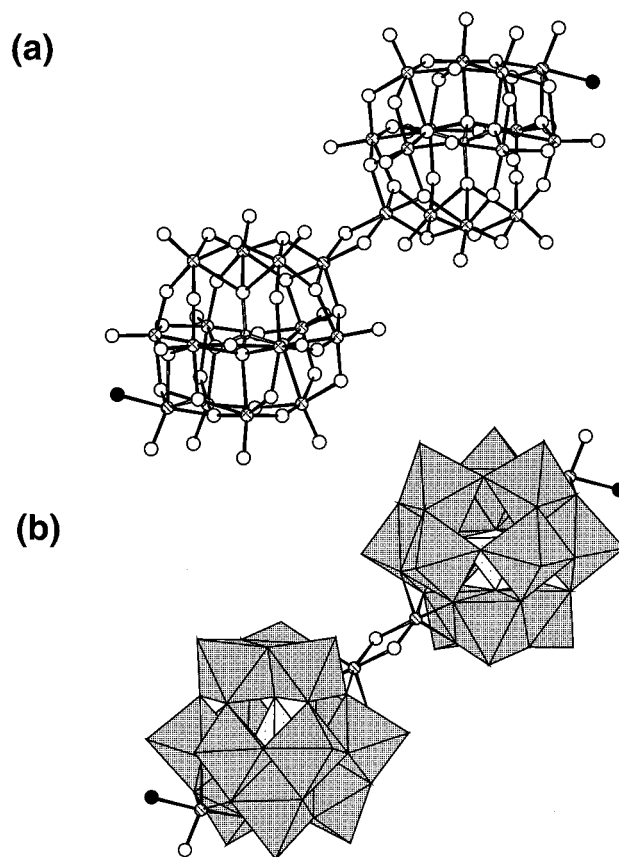


Figure 4. (a) Ball-and-stick representation of $[\text{Si}_2\text{Mo}_{28}\text{O}_{84}(\text{H}_2\text{O})_2]^{6-}$ ($\text{Si}_2\text{Mo}_{28}$): O atoms of the water molecules, solid spheres. (b) Polyhedral representation.

units, as in $[\text{H}_4\text{As}^{\text{III}}_2\text{As}^{\text{V}}\text{Mo}^{\text{V}}_8\text{Mo}^{\text{VI}}_4\text{O}_{40}]^{-}$,²⁸ or $\{\text{As}^{\text{VO}}\}$ units, as in $[\text{H}_{12}\text{AsV}_{12}\text{O}_{40}(\text{As}^{\text{VO}})]^{3-}$.²⁹ To our knowledge, if we except the $[\text{PMo}_{14}\text{O}_{44}]^{4-}$ anion, once mentioned by Zubieta et al.²³ but never published, SiMo_{14} is the first example of a reduced Keggin anion with $\{\text{MoO}_2\}$ capping subunits.

Structure of the Dimerized Polyanion $[\text{Si}_2\text{Mo}_{28}\text{O}_{84}(\text{H}_2\text{O})_2]^{6-}$ ($\text{Si}_2\text{Mo}_{28}$). The heteropolyanion $\text{Si}_2\text{Mo}_{28}$ is formed by the linking of two identical SiMo_{14} anions (related by a center of inversion) by the two terminal oxygen atoms of the capping $\{\text{MoO}_2\}$ units, as shown in Figure 4. Bond valence sum calculations indicate that the bridging oxygen atom between the two *capping* and *bridging* $\{\text{MoO}_2\}$ units is an oxo ligand; this oxygen atom is not equally shared by the two molybdenum atoms: one Mo–O bond is short [1.698(10) Å] and is localized trans to a longer Mo–O bond [2.029(9) Å], while the other is far longer [2.182(10) Å] and is also trans to a shorter one [1.959(9) Å]. In the *capping* and *nonbridging* $\{\text{MoO}_2\}$ units, the same trend is observed, with one short Mo–O_t bond [1.698(10) Å] and one long Mo–O_t bond [2.197(11) Å]. The longest Mo–O_t bond indicates that the corresponding O_t atom could be the oxygen of a water molecule. A comparison of the Mo···Mo distances (Table 2) between edge-sharing and corner-sharing octahedra in the Keggin core of $\text{Si}_2\text{Mo}_{28}$ with those observed in the $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ anion shows a net expansion of the Mo···Mo separations between the eight Mo atoms involved in bonding with the capping $\{\text{MoO}_2\}$ units. As the reduction has a slight contraction effect on the Mo···Mo distances between corner-sharing octahedra (Table 2), the expansion of these distances in $\text{Si}_2\text{Mo}_{28}$ is primarily due to the face-capping units. The effect

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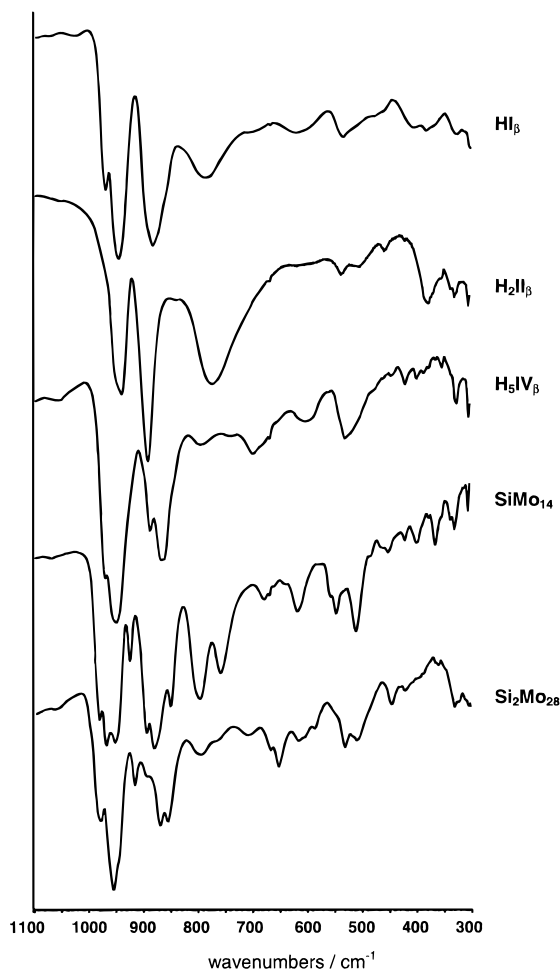
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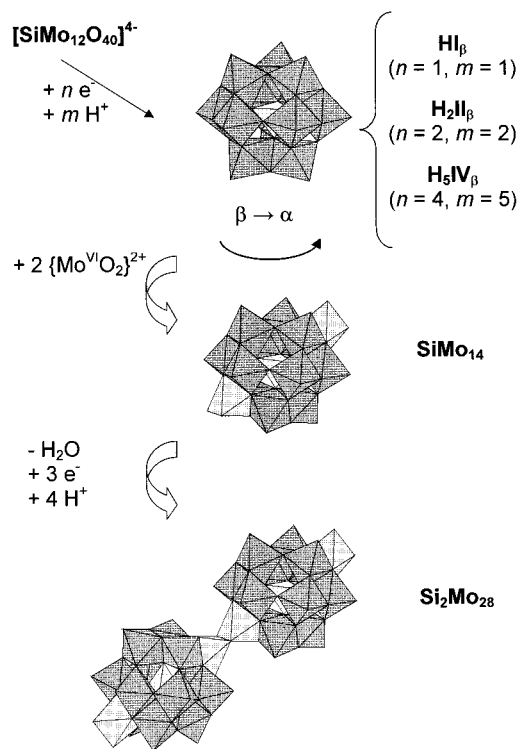
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Table 3. Absorption Frequencies between 1100 and 600 cm^{-1} , with Their Assignments, and Their Comparison with the Absorption Frequencies of α - and β -[SiMo₁₂O₄₀]⁴⁻³²

	β -[SiMo ₁₂ O ₄₀] ⁴⁻	α -[SiMo ₁₂ O ₄₀] ⁴⁻	HI _{β}	H ₂ II _{β}	H ₅ IV _{β}	SiMo ₁₄	Si ₂ Mo ₂₈
Mo—O _d	945	945, 940	971 (m), 950 (s)	942 (s)	970 (s), 953 (s)	983 (m), 971 (s), 953 (s), 925 (w)	986 (s), 958 (s), 919 (w)
Si—O _a	895	899	886 (s)	894 (s)	891 (m)	896 (s)	899 (w)
Mo—O _c —Mo edge-sharing	857	868		843 (w)	868 (s)	878 (s), 848 (s)	873 (m), 855 (m)
Mo—O _b —Mo corner sharing	800	795	789	776 (s)	796 (w), 701 (m)	791 (s), 758 (m), 683 (w)	796 (w)

**Figure 5.** Infrared spectra of the five polyanions.

of the extra capping groups is also evident on the lengthening of the Mo—O_b and Mo—O_c distances (Table 2) for the oxygen atoms bound to the capping {MoO₂} units, in a way analogous to the one evidenced for the protonation of the bridging oxygen atoms in HI _{β} , H₂II _{β} , and H₅IV _{β} . The remaining Mo—O_b distances are all shorter so that we can assume that none of the bridging oxygen atoms is protonated. This crystallographic study leads to the detailed formula [Si₂Mo^V₁₄Mo^{VI}₁₄O₈₄(H₂O)₂]⁶⁻ for anion Si₂Mo₂₈. The calculated bond numbers (5.25, 5.28) for the Mo atoms of the capping {MoO₂} units are significantly lower than those for the other molybdenum atoms (5.60–6.01) so that four of the “blue” electrons are assumed to be primarily localized on the capping fragments, the other being delocalized over the Mo atoms of the Keggin core. However, the adjacent Mo^V atoms of the two linked {MoO₂} units do not form Mo^V—Mo^V diamagnetic pairs. Indeed the Mo^{•••}Mo distance is 3.101 Å, in agreement with a nonbonding metal interaction. Mo^{•••}Mo distances between the molybdenum atoms of the Keggin core and the molybdenum atom of the extra capping {MoO₂}

**Figure 6.** Schematic stepwise growth process from the reduced β -SiMo₁₂ anion to the dimerized Si₂Mo₂₈ anion.

subunits (3.176–3.245 Å) are in the same range and are quite a bit shorter than the Mo^{•••}Mo separations within the Keggin core (Table 2). In this compound, the reduction of the bicapped SiMo₁₄ unit leads to a dimerization. A similar behavior has been reported for mixed molybdovanadate Keggin anions. Under mild conditions, the highly charged Keggin units [VMo^{VI}₈V^{IV}₄O₄₀]¹¹⁻ polymerize via {V₂(μ O)₂}⁴⁺ groups,³⁰ while under hydrothermal conditions, the dimerized [Mo₁₆V₁₄O₈₄]¹⁴⁻ anion is formed.³¹

Infrared Spectra. The infrared spectra of the five compounds differ in the region 1100–300 cm^{-1} (Figure 5). The vibrations of the tetramethylammonium cations are observed for all compounds at about 1400 cm^{-1} . The main absorption bands with their respective assumed assignments are given in Table 3 and are compared to the vibration frequencies of the α - and β -[SiMo₁₂O₄₀]⁴⁻ anions.³² Some trends can be given: the overall IR spectra of HI _{β} , H₂II _{β} , and H₅IV _{β} are similar to that of β -[SiMo₁₂O₄₀]⁴⁻, with three main bands at about 945 cm^{-1} [ν (Mo—O_d)], 900 cm^{-1} [ν (Si—O_a)], and 800 cm^{-1} [ν (Mo—O_b—Mo)]. The degree of reduction has a pronounced effect. The intensity of the Si—O band decreases with the number of “blue”

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electrons, from HI_β to $\text{H}_2\text{II}_\beta$ and $\text{H}_5\text{IV}_\beta$. A similar observation has been reported for the reduced derivatives of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$.¹⁸ In the IR spectra of SiMo_{14} and $\text{Si}_2\text{Mo}_{28}$, the Si–O band is also weaker than in the oxidized related compound α - $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$,³² and the number of bands in the expected range for Mo–O vibrations (1000 – 500 cm^{-1}) is greater than for the SiMo_{12} anions.

Conclusion. This work illustrates that Keggin discrete structures can be extended to polymeric material via reduction–condensation processes. The structural relationships between the monomeric β - $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ anion, with different reduction states, the bicapped anion, and the dimerized species are shown in Figure 6. By reduction of the β - $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ anion, the nucleophilic character of the bridging oxygen atoms is enhanced to lead to weak acidities. Such a behavior was previously reported by Massart et al., who electrochemically established the different reduction and protonation states of α - and β - $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$. In these reduced Keggin derivatives, the charge increase is balanced by protons attached to the doubly bridging oxygen atoms as shown by the characterizations of the β - $[\text{HSiMo}_{12}\text{O}_{40}]^{4-}$, β - $[\text{H}_2\text{SiMo}_{12}\text{O}_{40}]^{4-}$, and β - $[\text{H}_5\text{SiMo}_{12}\text{O}_{40}]^{3-}$ anions. For the four-electron-reduced species, the anionic charge is compensated either by protons or by two electrophilic $\{\text{MoO}_2\}^{2+}$ groups, according to the conditions of synthesis (pH, temperature). The first case leads to β - $[\text{H}_5\text{SiMo}_{12}\text{O}_{40}]^{3-}$ while the second one is encountered in the bicapped α - $[\text{SiMo}_{14}\text{O}_{44}]^{4-}$ anion. At high temperature and low

pH, the Keggin unit is first reduced and then the Mo atoms of the capping units to give a hypothetical five-electron reduced-Keggin structure with two $\{\text{Mo}^{\text{V}}\text{O}_2\}$ capping units. The electron-rich species dimerize to form $[\text{Si}_2\text{Mo}_{28}\text{O}_{84}(\text{H}_2\text{O})_2]^{6-}$. These results illustrate that self-condensation between the well-known Keggin structures can be carried out through sequences of reduction and condensation. Hydrothermal techniques have proved here to be effective in the synthesis of new polyoxometalates. For these mixed-valence heteropolyblue systems, a more rationalized process of synthesis would now merit development. Indeed, the reduction–condensation steps could be monitored under milder conditions such as electrolysis at controlled potential, in the presence of electrophilic oxocations. These concepts already extensively developed by Müller et al. for the molecular growth of giant polyoxomolybdates, until Mo_{248} , could be used to design complex frameworks, based on covalent assemblies of preformed molecular entities.

Acknowledgment. The authors thank Prof. Dr. A. Müller for allowing D.E. to work in Institut Lavoisier for a few months. M. Nogues (Université de Versailles, France) is gratefully acknowledged for SQUID magnetic measurements.

Supporting Information Available: X-ray crystallographic files, in CIF format, for HI_β , $\text{H}_2\text{II}_\beta$, $\text{H}_5\text{IV}_\beta$, SiMo_{14} , and $\text{Si}_2\text{Mo}_{28}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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