amenable to scale-up, geared to provide access to analogues, and involves only one protecting-group manipulation. [13]

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[13] Although the plant O*ttelia alismoides* is regarded as a weed and is widely distributed along irrigation canal linings and rice fields in the Afro-Asian region, otteliones A and B are present only at ppm levels; thus synthetic access through practical routes is necessary to evaluate their biological potential.

$[\varepsilon\text{-PMo}_{12}\text{O}_{36}(\text{OH})_4\{\text{La}(\text{H}_2\text{O})_4\}_4]^{5+}$: The First ε-PMo$_{12}O_{40}$ Keggin Ion and Its Association with the Two-Electron-Reduced α-PMo$_{12}$O$_{40}$ Isomer

Pierre Mialane, Anne Dolbecq, Laurent Lisnard, Alain Mallard, Jérôme Marrot, and Francis Sécheresse*

Dedicated to Professor Dr. Gilbert Hervé

Polyoxometalates, often considered as soluble metal oxides, have long attracted interest because of their large field of applications, especially in the domain of heterogeneous catalysis.[1] The famous Keggin ion $[\alpha\text{-PMo}_{12}\text{O}_{40}]^{3-}$ was isolated nearly 200 years ago. Isomerization formally results from successive 60° rotations of the four basic Mo_3O_{13} groups. Although the five isomers α, β, γ, δ, and ε of the Keggin structure have been postulated, only the α[2] and β[3] isomers of $\text{PMo}_{12}\text{O}_{40}$ have been structurally characterized to date. However, the ε-Keggin structure has been encountered in related compounds which are either polyoxocations, with an $\text{Al}^{\text{III}}_{12}$ core and a central tetrahedral Al^{III},[4] Ga^{III}, or Ge^{III}[5] center, or polyoxoions with $\text{Mo}^{\text{V}}_{12}$ and V^{V}_{12} cores. In the case of Mo and V derivatives,[6] the highly negatively charged structure is stabilized by electrophilic capping groups. The $\text{Mo}^{\text{V}}_{12}\text{O}_{40}$ skeleton has been crystallographically characterized in four polyoxometalates: the $[(\text{C}_5\text{Me}_5\text{Rh}^{\text{III}})_8(\text{Mo}^{\text{V}}_{12}\text{O}_{36})(\text{Mo}^{\text{VI}}\text{O}_4)]^{2+}$ complex[7] has a central $\text{Mo}^{\text{VI}}\text{O}_4^{\,2-}$ tetrahedron and eight Rh^{III} capping centers, the $[\text{NaMo}_{16}(\text{OH})_{12}\text{O}_{40}]^{7-}$[8, 9] and $[\text{H}_2\text{Mo}_{16}(\text{OH})_{12}\text{O}_{40}]^{6-}$[8] polyoxometalates are stabilized by four capping $\text{Mo}^{\text{VI}}\text{O}_3$ units and have a central cavity encapsulating a sodium cation and two protons, respectively. Finally, the most recent example is the $[\text{Mo}_{12}\text{O}_{30}(\text{OH})_{10}\text{H}_2\{\text{Ni}(\text{H}_2\text{O})_3\}_4]$ cluster[10] with two central protons and four Ni^{II} capping centers. These compounds highlight the capacity of the ε-$\{\text{Mo}_{12}\text{O}_{40}\}$ core to encapsulate various guests. We report here the synthesis and characterization of the first ε-Keggin cation with a central phosphorous atom, stabilized by four $\{\text{La}(\text{H}_2\text{O})_4\}^{3+}$ capping groups. This cation was isolated in the three different salts **1**, **2** and **3**:

$[\varepsilon\text{-PMo}_{12}\text{O}_{36}(\text{OH})_4\{\text{La}(\text{H}_2\text{O})_4\}_4]\text{Br}_5\cdot 16\,\text{H}_2\text{O}$ **1**

$[\varepsilon\text{-PMo}_{12}\text{O}_{36}(\text{OH})_4\{\text{La}(\text{H}_2\text{O})_{2.5}\text{Cl}_{1.25}\}_4]\cdot 27\,\text{H}_2\text{O}$ **2**

$\text{K}_3[\varepsilon\text{-PMo}_{12}\text{O}_{36}(\text{OH})_4\{\text{La}(\text{H}_2\text{O})_{4.25}\text{Cl}_{0.75}\}_4][\alpha\text{-PMo}_{12}\text{O}_{40}]\cdot 28\,\text{H}_2\text{O}$ **3**

Compound **1** is the bromide salt of the $[\varepsilon\text{-PMo}_{12}\text{O}_{36}(\text{OH})_4\{\text{La}(\text{H}_2\text{O})_4\}_4]^{5+}$ polyoxocation. Compounds **2** and **3** have chloride ions directly bound to the capping La^{3+} centers; **2** is a neutral compound while **3** has an $[\alpha\text{-PMo}_{12}\text{O}_{40}]^{5-}$ ion as the counterion.

Compounds **1** and **2** were characterized by ^{31}P NMR, IR, and UV/Vis spectroscopy, elemental analysis, potentiometric

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titrations, and the structures of compounds **1**–**3** were determined by single-crystal X-ray diffraction.[11] In a typical experiment, a solution of Mo^{V}, freshly prepared by the reduction of sodium molybdate by hydrazine in acidic medium, is mixed with a solution of $Mo^{VI}O_4^{2-}$, $H_2PO_4^-$ ions and an excess of La^{3+} ions. Red cubic crystals of **1** form by slow evaporation of an hydrobromic acid solution while crystals of **2** are obtained from a reaction mixture containing chloride ions. The blue color of the filtrate can be attributed to the presence of either high-nuclearity species often known as "molybdenum blues" and extensively studied by Müller et al.[12] or to partially reduced $PMo_{12}O_{40}$ species. Attempts to synthesize compounds **1** and **2** in absence of $Mo^{VI}O_4^{2-}$ ions have failed. Indeed, potentiometric titrations have shown that both compounds contain 8 Mo^{V} and 4 Mo^{VI} centers. This result is unexpected, all the previously characterized ε-Keggin molybdenum complexes containing only Mo^{V} ions. As no intervalence $Mo^{V} \rightarrow Mo^{VI}$ charge-transfer bands have been observed by electronic absorption spectroscopy (**1** and **2** are red), it is assumed that the Mo^{V} centers form Mo^{V}–Mo^{V} diamagnetic pairs. Both **1** and **2** contain the ε-$Mo_{12}O_{40}$ core, derived formally from the α-Keggin isomer by rotation of all four Mo_3O_{13} groups by 60° around the C_3 axes. The twelve Mo ions lie on the vertices of a truncated tetrahedron (Figure 1 b) and form six Mo–Mo pairs. Because of the cubic symmetry of the structure, the four Mo^{V}–Mo^{V} and the two Mo^{VI}–Mo^{VI} pairs have been found disordered ($d_{Mo-Mo} = 2.697(3) - 2.780(1)$ Å). The central cavity accommodates a PO_4 tetrahedron with P–O bonds (1.59(1) Å) in the expected range. The overall T_d symmetry of the ε-$\{Mo_{12}O_{40}\}$ structure is maintained by the aggregation of four stabilizing La^{3+} units on the four faces of the truncated tetrahedron defined by the twelve Mo centers (Figure 1 a). The La^{3+} ions are bound to the Keggin core by three oxygen atoms. In **1**, their coordination sphere is completed by four water molecules, three of which are disordered over two positions. Seven-coordinate La^{3+} ions are not commonly observed but a few examples have been described.[13] Furthermore, in **1**, five disordered bromide ions are located in the voids left by the Keggin polyoxocations. The overall charge of the Keggin unit is thus 5+ which implies the presence of four protons on four of the twelve μ_2-O atoms. Because of the high symmetry of the cation, these protons cannot be located and are assumed to be delocalized on the overall structure. The detailed formula of the ε-Keggin cation in **1** is thus [ε-$PMo_8^{V}Mo_{36}^{VI}O_{36}(OH)_4\{La(H_2O)_4\}_4$. In **2**, the chloride counterions, which are better ligands than bromide ions, are directly bound to the La^{3+} ions and substitute five of the disordered water molecules ($d_{La-Cl} = 2.75(1)$ Å).

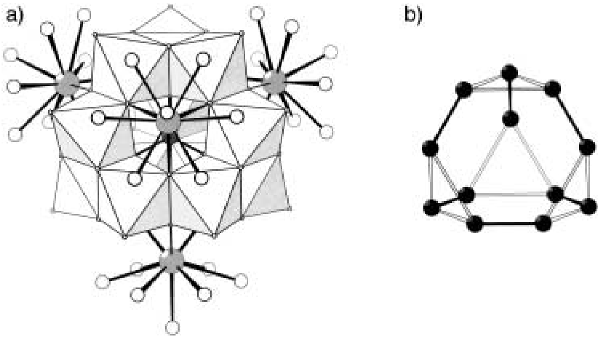

Figure 1. a) Polyhedral representation of the ε-Keggin core in **1** capped with four $\{La(H_2O)_4\}^{3+}$ groups. Six of the terminal oxygen atoms of the water molecules on the La^{3+} ions have half occupancy factors; b) disposition of the twelve Mo atoms, the Mo–Mo pairs are linked in black.

Compound **1** dissolves readily in water to give dark red solutions. The ^{31}P NMR spectrum reveals two resonances δ_1 and δ_2, located at $\delta = 1.37$ and 0.91, respectively, and with relative intensities 1:5 (Figure 2 a). The evolution of the NMR spectrum after the addition of increasing amounts of $LaCl_3$ in the solution (Figure 2) has been compared to a similar experiment where $LaCl_3$ is replaced by NaCl. When NaCl is added, the spectrum remains unchanged while the addition of $LaCl_3$ has a dramatic effect on the δ_1 line, which progressively decreases and completely disappears. These results show that the Keggin ion is involved in an equilibrium with La^{3+} ions. Considering the evidence of only two ^{31}P NMR peaks, we can propose the following equilibrium [Eq. (1)].

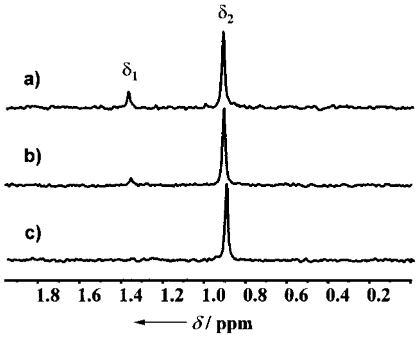

Figure 2. ^{31}P NMR spectra of an aqueous solution of [ε-$PMo_{12}O_{36}(OH)_4\{La(H_2O)_4\}_4]^{5+}$ (ε-PMo_{12}) to which $LaCl_3$ was added; the ratios of initial concentrations were a) $[La^{3+}]:[\varepsilon\text{-}PMo_{12}]^0 = 0:1$, b) $[La^{3+}]:[\varepsilon\text{-}PMo_{12}]^0 = 0.3:1$, c) $[La^{3+}]:[\varepsilon\text{-}PMo_{12}]^0 = 0.8:1$.

$$[\varepsilon\text{-}PMo_{12}O_{36}(OH)_4\{La(H_2O)_4\}_4]^{5+} \rightleftarrows [\varepsilon\text{-}PMo_{12}O_{36}(OH)_4\{La(H_2O)_4\}_3]^{2+} + La^{3+} + 4\,H_2O \qquad (1)$$

The smallest peak (δ_1) is thus attributed to the species with three capping La^{3+} ions while the remaining peak (δ_2) is assigned to the parent ion. From these data the value of the related apparent constant of the equilibrium is $K = 2.4 \times 10^{-4}\,mol\,L^{-1}$. Furthermore, as **1** and **2** have identical ^{31}P NMR spectra, it is thus likely that in water the chlorine atoms of **2** are rapidly exchanged with water molecules to give the fully hydrated ions.

When a solution of **2** is left in air at room temperature for several days, a brown powder, totally insoluble in water and in the most usual organic solvents, slowly precipitates which shows that the ε-Keggin ion can be readily oxidized. A few dark brown crystals of the oxidation product **3** have been obtained from an aqueous KCl solution of **2**. A single-crystal analysis has shown that, unexpectedly, **3** is a composite of the ε cation and an α-Keggin isomer of $PMo_{12}O_{40}$. As the nonreduced α isomer (0_α) readily decomposes at pH > 2 and the four-electron-reduced β isomer (IV_β) is more stable than the IV_α isomer in aqueous solution,[14] it can be postulated that in **3** the α isomer is the two-electron-reduced $[\alpha\text{-PMo}^{\mathrm{V}}_{2}\text{Mo}^{\mathrm{VI}}_{10}\text{O}_{40}]^{5-}$ (II_α) Keggin ion. Both isomers, the ε- and α-Keggin ions thus play the role of counterions to each other, an unprecedented feature in the chemistry of polyoxometalates. Three chlorine atoms have been found disordered on the four capping La^{3+} groups, which can be explained by the high concentration of chlorine ions in the medium (0.2 M). Concomitantly, three disordered potassium ions have been located in the structure. The geometrical features of the ε-Keggin ions, especially the mean values for the bond valence sum calculations[15] on the μ_2-O atoms, are maintained, which shows that the degree of protonation of the ε-Keggin ion in **2** remains unchanged in **3**. In the α-Keggin ion, the two Mo^{V} units among the twelve Mo centers are delocalized on the overall structure, as usually observed for two-electron-reduced Keggin structures.[2c, 16] The 3D structure of **3** is remarkable, columns of ε-Keggin polyoxometalates, positively charged, alternate with columns of α-Keggin ions, negatively charged (Figure 3). The positions of the ions, along the *c* axis, are shifted from a cationic column to an anionic column, to optimize the cation–anion interactions and obtain the most compact structure. The 3D arrangement can thus be described as a pseudo CsCl structure, which is not surprising considering that the anionic and cationic species can be approximated to spheres of comparable radii (~6 Å).

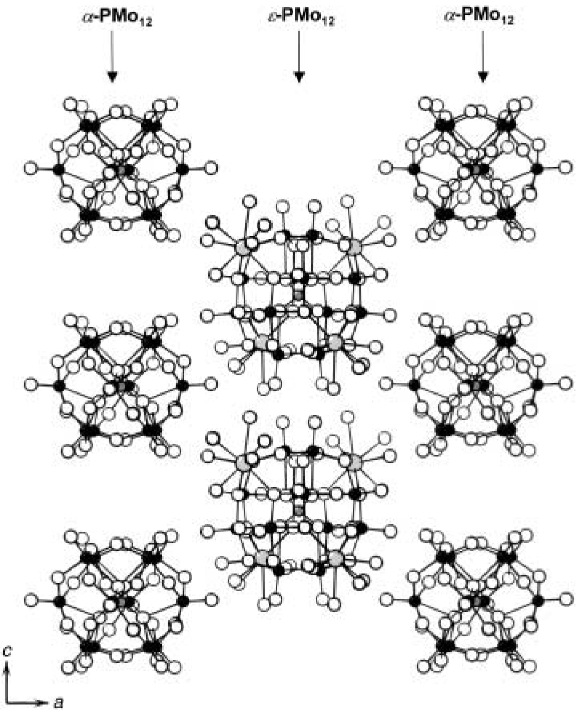

Figure 3. View of the columns of ε- and α-Keggin ions in **3**.

The mechanism of the formation of **3** from **2** involves several intermediates but it can be assumed that in solution, as shown by the NMR spectroscopic studies, two species are in equilibrium, one with four and the other with three capping La^{3+} ions. The loss of one capping La^{3+} ion destabilizes the ε cation which is more easily oxidized in solution by air, and slowly decomposes to form the II_α Keggin anion. This anion, once formed, precipitates as the totally insoluble salt **3**. This hypothesis was confirmed by the direct synthesis of a mixed salt of the two Keggin derivatives by adding a stoichiometric amount of II_α to a solution of **2**, stabilized by a small quantity of $LaCl_3$. A microcrystalline brown precipitate, compound **4**, immediately formed the IR spectrum and X-ray diffraction powder patterns of which are similar to the experimental IR spectrum and to the simulated powder pattern, respectively, of **3** (Figure 4). The microanalysis of **4** is consistent with the formula $[\varepsilon\text{-PMo}_{12}\text{O}_{36}(\text{OH})_4\{\text{La}(\text{H}_2\text{O})_4\}_4][\alpha\text{-PMo}_{12}\text{O}_{40}]\cdot 31\,\text{H}_2\text{O}$. Compound **4** is thus the analogue of **3** without chloride and potassium ions. Both compounds crystallize in the same crystal lattice, imposed by the large Keggin polyanions and polycations. Similarly **4** can be also synthesized by adding a solution of II_α to an aqueous solution of **1**.

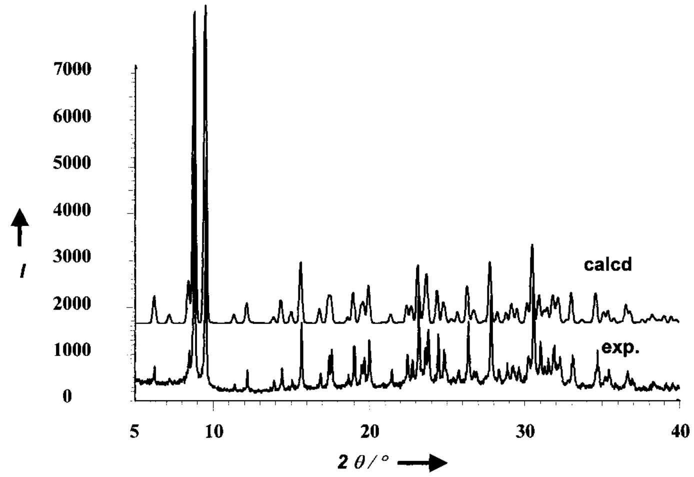

Figure 4. Comparison of the experimental X-ray diffraction powder pattern of **4** and the simulated powder pattern of **3**.

In summary, a novel polyoxocation with the rare ε-Keggin structure has been obtained and characterized. The polyoxocation is soluble in water and can be precipitated with the two-electron-reduced $[\alpha\text{-PMo}_{12}\text{O}_{40}]^{5-}$ Keggin ion to form a composite salt. The crystallization of the ε-Keggin ion in concentrated chloride solutions has shown that the water molecules bound to the lanthanum ions are labile and can be substituted by chloride ions. The functionalization of the ε-Keggin ion could thus be possible by reaction with various ligands, either inorganic (SCN^-, CN^- …) or organic.

Experimental Section

1: A solution of $\{Mo_2O_4(H_2O)_4\}^{2+}$ 0.2 M was prepared by dissolving $Na_2MoO_4\cdot 2H_2O$ (0.5 g, 2 mmol) in 4 M HBr (10 mL) followed by the addition of $N_2H_4\cdot 2H_2O$ (26 μL, 0.5 mmol). The solution was stirred overnight. To this red solution 1 M Na_2MoO_4 (0.5 mL, 0.5 mmol) and 0.1 M NaH_2PO_4 (2.1 mL, 0.21 mmol) was added dropwise. Meanwhile, a solution of La^{3+} ions was obtained by dissolution of La_2O_3 (4.07 g, 12.5 mmol) in HBr 4 M (18.75 mL, 75 mmol). The pH value was adjusted to 1.5 by addition of 8 M NaOH. The dark green reaction mixture was stirred for 15 min, filtered, and then allowed to stand at room temperature for crystallization. After two weeks dark red cubic crystals of **1** (0.114 g, 15 % yield, based on

Mo) suitable for X-ray diffraction were collected by filtration and washed with ethanol. It should be noted that the yield of the synthesis is not significantly improved when a stoichiometric amount of Mo^{VI} ions is added in the synthesis. IR: $\tilde{\nu} = 999$(w), 989(w), 966(w), 930(s), 917(s), 811(m), 766(s), 748(sh), 693(w), 603(m), 518(w), 503(w), 477 cm^{-1} (w); UV/Vis spectra (H_2O): $\lambda_{max}(\varepsilon) = 432$ (14100), 292 nm (42200); elemental analysis calcd (%) for $H_{72}Br_5La_4Mo_{12}O_{72}P$: Br 11.78, La 16.39, Mo 33.97, P 0.91; found Br 11.13, La 15.81, Mo 34.01, P 1.08.

2: A solution of $\{Mo_2O_4(H_2O)_4\}^{2+}$ 0.2 M was prepared by dissolving $Na_2MoO_4 \cdot 2H_2O$ (0.5 g, 2 mmol) in 4 M HCl (10 mL) followed by the addition of $N_2H_4 \cdot 2H_2O$ (26 µL, 0.5 mmol). The solution was stirred overnight. To this red solution was added dropwise 1 M Na_2MoO_4 (0.5 mL, 0.5 mmol), 0.1 M NaH_2PO_4 (2.1 mL, 0.21 mmol), and then $LaCl_3 \cdot 7H_2O$ (9.28 g, 25 mmol) dissolved in water (30 mL). The pH value was adjusted to 1.5 by addition of 8 M NaOH. The dark green reaction mixture was stirred for 15 min, filtered and then allowed to stand at room temperature for crystallization. After two weeks dark red cubic crystals of **2** (0.148 g, 21% yield, based on Mo) suitable for X-ray diffraction studies were filtered and washed with ethanol. The IR spectra of **1** and **2** have the same characteristic bands; elemental analysis calcd (%) for $H_{100}Cl_5La_4Mo_{12}O_{86}P$: Cl 5.23, La 16.38, Mo 33.95, P 0.91; found Cl 5.78, La 16.39, Mo 33.52, P 1.32.

Single crystals of **3**: Solid KCl (0.149 g, 2.0 mmol) was added to a solution of **2** (0.050 g, 1.45×10^{-5} mol) dissolved in water (10 mL). The solution (pH 3.4) was stirred for 5 min and then allowed to stand in air. After a week a few dark brown parallelepiped crystals of **3**, mixed with an unidentified brown powder, were collected by filtration, washed with ethanol and dried with diethyl ether.

II_{α}: The two-electrons-reduced $[\alpha\text{-}PMo_{12}O_{40}]^{5-}$ (II_{α}) ion was synthesized by electrolysis on a platinum electrode at a steady potential (−0.1 V versus standard calomel electrode (SCE)) of a solution of $[PMo_{12}O_{40}]^{3-}$ in $HClO_4$ 1 M/1,4-dioxane (50/50).[14] The degree of reduction was controlled by polarography. The acid salt $H_5II_{\alpha} \cdot {\sim}20H_2O$ was precipitated with concentrated HCl, filtered, and dried in air.

4: As solutions of **2** have been found to be air sensitive, the reaction was performed under a nitrogen atmosphere using standard Schlenk techniques. A solution of $H_5II_{\alpha} \cdot {\sim}20H_2O$ (0.065 g, 2.95×10^{-5} mol) in degassed water (5 mL) was added dropwise to a solution of **2** (0.100 g, 2.95×10^{-5} mol) and $LaCl_3 \cdot 7H_2O$ (0.011 g, 2.95×10^{-5} mol) in degassed water (5 mL). A dark brown precipitate (0.130 g, yield 87%) immediately formed, which was collected by filtration and washed with water and ethanol. IR: $\tilde{\nu} = 1055$(w), 1018(w), 985(w), 963(w), 935(s), 904(sh), 863(sh), 817(s), 766(s), 693(w), 603(m), 518(w), 503(w), 477 cm^{-1} (w); elemental analysis calcd (%) for $H_{102}La_4Mo_{24}O_{127}P_2$: La 10.88, Mo 45.12, P 1.21; found La 10.90, Mo 45.04, P 1.45, Cl 0.04.

Chemical analyses: redox back titrations for the determination of the amount of Mo^V ions is based on the oxidation of Mo^V by Ce^{4+} ions. The sample (about 30 mg) was dissolved in water (20 mL) and excess Ce^{4+} ion solution (0.05 M); the excess Ce^{4+} ion was titrated potentiometrically with Fe^{2+} ions (0.05 M) using a 702 SM Titrino.

NMR measurements: ^{31}P NMR spectra were recorded at 278 K on a Bruker AC-300 spectrometer operating at 121.5 MHz in 5 mm tubes. ^{31}P chemical shifts are referenced to the external standard 85% H_3PO_4. The initial concentration of **1** was $[\varepsilon\text{-}PMo_{12}]^0 = 8.5\ 10^{-3}$ M. Increasing amounts of a solution of $LaCl_3$ ($[La^{3+}]^0 = 0.17$ M) were added in the NMR tube.

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[11] Crystal data and structure refinements for **1**: a dark red cubic crystal ($0.18 \times 0.18 \times 0.16$ mm) was analyzed with a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector using $Mo_{K\alpha}$ monochromatized radiation ($\lambda = 0.71073$ Å). Cubic, space group $P\bar{4}3m$, $a = 12.2256(1)$ Å, $V = 1827.30(3)$ Å^3, $Z = 1$, $\rho_{calcd} = 2.757$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 7.105$ mm^{-1}, $F(000) = 1370$, 13173 reflections measured, of which 1030 were independent, 57 refined parameters, $R = 0.0572$, $wR_2 = 0.1474$. **2**: a dark red crystal ($0.34 \times 0.22 \times 0.22$ mm); cubic, space group $P\bar{4}3m$, $a = 12.4193(1)$ Å, $V = 1915.54(3)$ Å^3, $Z = 1$, $\rho_{calcd} = 2.437$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 4.344$ mm^{-1}, $F(000) = 1280$, 8636 reflections measured, of which 990 were independent, 69 refined parameters, $R = 0.0701$, $wR_2 = 0.1766$. **3**: a dark brown plate ($0.14 \times 0.12 \times 0.04$ mm); tetragonal, space group $P\bar{4}$, $a = 20.2354(2)$, $c = 12.3785(2)$ Å, $V = 5068.6(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 3.182$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 4.857$ mm^{-1}, $F(000) = 4460$, 23474 reflections measured, of which 7289 were independent, 399 refined parameters, $R = 0.0657$, $wR_2 = 0.1248$. All the molybdenum and phosphorus atoms of the Keggin ions were refined anisotropically while the potassium, oxygen, and chlorine atoms were refined by using isotropic temperature factors. For **1**, **2**, and **3**, data reduction was performed with the SAINT software. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program based on the method of Blessing. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELX-TL package. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-412375 (**1**), -412376 (**2**), and -412377 (**3**).

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