Antimony-Substituted Keggin-Type Polyoxomolybdates: Polar Crystals and Catalytic Oxidative Dehydrogenation of Alcohols

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An antimony-substituted polyoxomolybdate, $[PSb^{III}(H_2O)Mo_{11}O_{39}]^{4-}$, of the α-Keggin structure, has been synthesized. Although the molecular structure is typical, we have found from the analysis of the X-ray diffraction data that the crystal is anisotropic with alignment of the molecular units so that the substituted antimony atoms are all directed along the polar *c* axis and on the same side of the molecular unit. UV/Vis, ESR and magnetic susceptibility data support a formulation of $[PSb^{III}(H_2O)Mo_{11}O_{39}]^{4-}$ whereby there is partial electron delocalization with some formation (10–20%) of Mo^V. Oxidation of $[PSb^{III}(H_2O)Mo_{11}O_{39}]^{4-}$ with ozone or bromine yields the oxidized species $[PSb^V(O)Mo_{11}O_{39}]^{4-}$ and $[PSb^V(Br)Mo_{11}O_{39}]^{3-}$. In the anaerobic oxydehydrogenation of alcohols, $[PSb^V(O)Mo_{11}O_{39}]^{4-}$ is more active than $[PSb^V(Br)Mo_{11}O_{39}]^{3-}$. Catalytic aerobic oxidation of benzylic alcohols to aldehydes was also possible with no over-oxidation and formation of carboxylic acids.

Introduction

Mixtures of metal oxides containing both main group and transition metal elements are very important materials used as catalysts for heterogeneous, gas phase oxidative transformations. Such oxidative transformations include oxydehydrogenation, oxygenation and ammonoxidation reactions. Conceptually, polyoxometalates or heteropolyanions may be considered to be soluble analogs of such metal oxides and have been shown to be of general interest as catalysts for low temperature, homogeneous, liquid phase oxidation reactions.[1−6] Essentially, research carried out to date in this context can be divided into two main groups. In one research area, transition metal-substituted polyoxotungstates are used as catalysts. Here, it has been convenient to picture the catalytic process by proposing the activation of an oxidant such as iodosobenzene,[7−9] hydroperoxide,[10−18] periodate,[19−22] *N*-oxide,[23] or molecular oxygen[24−26] at the transition metal center which is "ligated" by a lacunary polyoxotungstate. In the second set of investigations, polyoxomolybdates and polyoxovanadomolybdates of the Keggin structure with high redox potentials, almost invariably $[PV_xMo_{12-x}O_{40}]^{q-}$ ($x = 0, 1, 2$), are used as catalysts. Significant applications of these compounds include their use in place of copper salts in Wacker-type reactions,[27−28] in oxydehydrogenation reactions[29−33] and most recently in the oxygenation of hydrocarbons.[34]

Since mixed metal oxides containing antimony oxide often play an important role in heterogeneous oxidation catalysis, we sought to prepare and characterize the first polyoxomolybdates of the Keggin structure substituted in the addenda position by Sb^{III} and Sb^V atoms. The catalytic activity of these polyoxoantinomatomolybdates was investigated and compared to the well-known polyoxovanadomolybdates. The literature that describes antimony-containing polyoxometalates is rather scant. Originally little was known about the compositions and structures of Sb^{III}-containing polyoxotungstates.[35−37] More recently, large clusters of polyoxotungstates containing Sb^{III} in the heteroatom but not addenda positions have been prepared and structurally determined.[38−39] Also, it has been shown that antimony *counter cations* have a stabilizing effect on polyoxometalates at high (>400 °C) temperatures.[40−42]

Results and Discussion

Synthesis, Structure Determination and Characterization of $[PSb^{III}(H_2O)Mo_{11}O_{39}]^{4-}$

The first approach taken to prepare phosphomolybdates with antimony substitution in the addenda position was by the classical synthesis whereby an acidified solution of molybdate, antimonate, and phosphate is extracted with diethyl ether. For example, Sb_2O_5 (5 mmol) in 50 mL concentrated HCl was refluxed until dissolution, followed by addition of Na_2HPO_4 (5 mmol in 10 mL H_2O), $Na_2MoO_4{\cdot}2H_2O$ (55 mmol in 40 mL H_2O) and 2.5 mL concentrated H_2SO_4 and heating at 90 °C for 1 h. The isolated polyoxometalate was shown by ICP-MS to contain only a very small amount of antimony with a P/Sb/Mo ratio of 1:0.04:12. Increasing the amount of Sb_2O_5 was to no avail. However, preparation of the antimony(III)- and antimony(V)-substituted phosphomolybdate is straightforward in nonaqueous media by insertion of $Sb(OAc)_3$ into the lacunary position of $[Q_4H_3PMo_{11}O_{39}]$ [$Q = (n\text{-}C_4H_9)_4N^+$], Equation (1).[43]

$$Q_4H_3PMo_{11}O_{39} \quad + \quad Sb(OAc)_3 \quad \xrightarrow[CH_3CN]{} \quad Q_4Sb(L)^{III}PMo_{11}O_{39}$$

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The reaction yielded, after recrystallization, dark green prisms of $Q_4PSb^{III}(H_2O)Mo_{11}O_{39}$ which were used for X-ray diffraction measurements. The compound crystallizes in the monoclinic space group C_c (No. 9) with two molecular formula units per asymmetric unit. For details of the structural analysis, see the Experimental Section, Table 1 and Supporting Information. The polyoxoanion itself has the usual α-Keggin-type structure. For one molecule of the asymmetric unit, the central phosphate moiety was well defined whereas for the other phosphate there was disordered oxygen coordination. Also there is coordination of a simple oxygen-containing ligand (assumed to be water) at the antimony position. Generally, in most monosubstituted Keggin structures, XMW_{11}, the substituted metal atom positions are fully disordered due to the cubic crystal structure.[44] Here, the lower monoclinic symmetry has allowed us to determine that the compound crystallizes anisotropically with the antimony atoms aligned along the polar *c* axis (Figure 1). The anisotropic antimony positions originally determined from the Patterson solution were confirmed by the observation that isotropic substitution into the structure at other positions, or assuming positional disorder of the antimony atom, led to statistically significantly poorer *R* values without the addition of extra parameters. Inspection of the packing revealed the anisotropic arrangement of the molecule with respect to the polar *c* axis. Importantly, this anisotropy is observed despite the fact that the larger Sb^{III} cation (0.80 Å vs. 0.60 Å for Mo^{VI})[45] is well accommodated in the addenda position of the Keggin compound without significantly distorting the molecular structure. The average bond lengths are $Mo-O_t = 1.686$ (range 1.65−1.74, s = 0.038), $Mo-O_c = 1.992$ (range 1.76−2.08, s = 0.104) and $Mo-O_e = 1.926$ (range 1.81−2.09, s = 0.091). The average bond lengths for the antimony position are $Sb-O_t = 1.72$, $Sb-O_c = 1.86$ and $Sb-O_e = 1.85$ and are not statistically different from those associated with molybdenum: that is, the Sb−O bonds lengths are within one standard deviation of those of the respective Mo−O bond lengths. In the past in mono-substituted Keggin compounds, such anisotropy has been observed only in two cases. In the first example, it was observed for the $[GaPbW_{11}O_{39}]^{7-}$ compound.[46] This Keggin species has a significantly distorted structure because of the much larger size of the Pb^{2+} cation[45] (W^{VI} = 0.58 Å vs. Pb^{II} = 1.18 Å), which might explain the anisotropic crystals formed. In the second instance, alignment is attained by formation of chains in manganese- and cobalt-substituted phosphotungstates. Bonds are formed due to displacement of the labile aquo ligand of the transition metal leading to chainlike polymeric structures with molecular units bridging oxo moieties, WO_t-M.[47−48] To reiterate, in this case the structure is not distorted, nor is there indication of intermolecular bonding.

Several additional lines of evidence support the substitution of Sb^{III} into the lacunary position of the polyoxomolybdate. First, the IR spectrum of $[PSb^{III}(H_2O)Mo_{11}O_{39}]^{4-}$ (Figure 2b) is similar to that of $[PMo_{12}O_{40}]^{3-}$ and significantly different from the spectrum of the lacunary species (Figure 2a). The four peak spectrum of the complete polyoxometalate is typical for Keggin structures of T_d symmetry. Second, the ^{31}P NMR spectrum of $[Q_4PSb^{III}(H_2O)Mo_{11}O_{39}]$ has a single peak at $\delta = -1.20$, whereas the peak for the lacunary $[Q_4H_3PMo_{11}O_{39}]$ is at $\delta = -4.82$. The cyclic voltammogram of $[PSb^{III}(H_2O)Mo_{11}O_{39}]^{4-}$ {0.5 mM $[Q_4PSb^{III}(H_2O)Mo_{11}O_{39}]$, 1 M QBF_4 in CH_3CN} shows a well-defined one- or two-electron Mo (VI → V) process that is very similar to that of $[PMo_{12}O_{40}]^{3-}$. No oxidation of antimony(III) to antimony(V) or reduction of antimony(V) to antimony(III) in the polyoxomolybdate was observed in the cyclic voltammograms in the interval +1.1 to −0.3 V.

We have formulated the Sb^{III}-substituted species as $[PSb^{III}(H_2O)Mo_{11}O_{39}]^{4-}$ indicating localization of the valence electrons on the antimony atom. This formulation is worthy of further comment. Thus, it is important to stress that upon addition of $Sb(OAc)_3$ to the lacunary substrate

Table 1. Crystallographic data for $[Q_4PSb^{III}(H_2O)Mo_{11}O_{39}]$

Space group	*Cc* (No. 9)
a, Å	45.6230 (7)
b, Å	14.1800 (2)
c, Å	26.4390 (4)
β, deg	95.8933 (8)
V, Å^3	17013.9 (4)
Z	4
$\rho_{calcd.}$, g cm^{-3}	1.821
μ(Mo-K_α), mm^{-1}	1.965
No. of unique reflections	10857
No. of reflections [$I \geq 2\sigma(I)$]	10443
R [$I \geq 2\sigma(I)$]	0.065
R (all data)	0.067

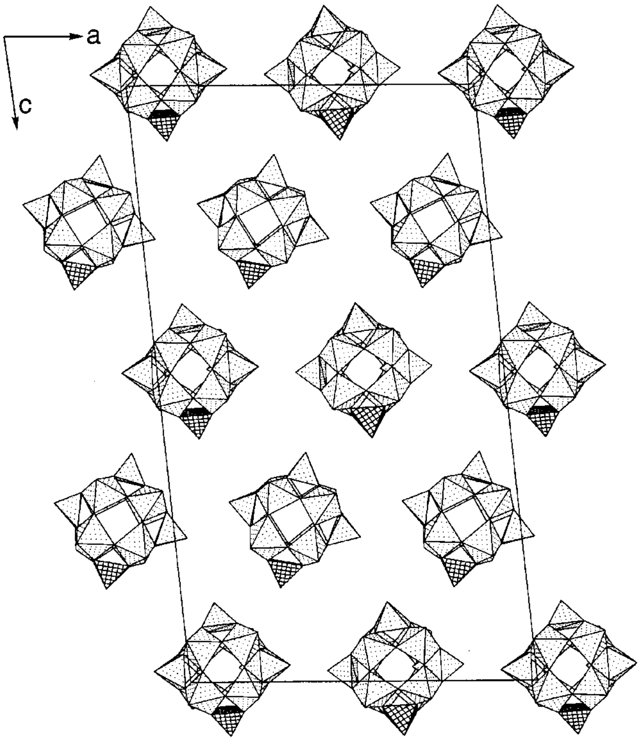

Figure 1. Structure of the inorganic sub-lattice in the *ac* plane; the Sb-containing polyhedra are hashed and the Mo-containing polyhedra are dotted

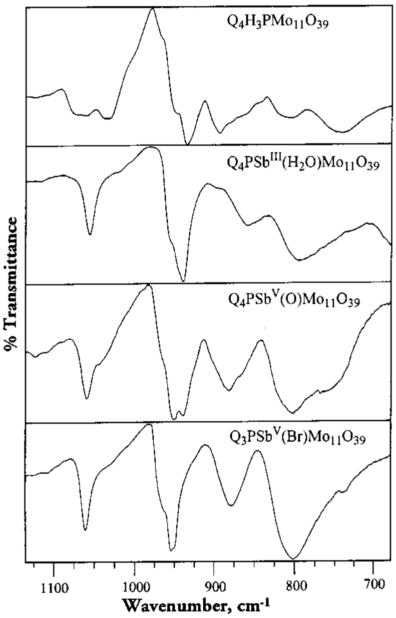

Figure 2. IR spectra of the various phosphoantimonatomolybdates

the solution became deep green, indicating reduction of the polyoxomolybdate and electron transfer (delocalization) from Sb^{III} (5s electrons) to Mo^{VI} (4d). In the UV/Vis spectrum of $[Q_4PSb^{III}(H_2O)Mo_{11}O_{39}]$ in acetonitrile the typical absorbance at ≈750 nm is observed. Importantly, however, the molar extinction coefficient ($\varepsilon = 0.17\ \text{mM}^{-1}\text{cm}^{-1}$) is one order of magnitude less than a one-electron-reduced $[PMo_{12}O_{40}]^{4-}$ ion prepared by addition of one equivalent of hydrazine to $[PMo_{12}O_{40}]^{3-}$. The intensity of the peak at ≈750 nm is a well-known measure of the degree of reduction of polyoxometalates.[49] Second, the ESR spectrum of $[Q_4PSb^{III}(H_2O)Mo_{11}O_{39}]$ in CH_3CN at 25 °C showed only a weak isotropic signal at the expected field,[50] $g = 1.937$, $A = 75$ G, which had about ≈5−10% of the intensity of $[PMo_{12}O_{40}]^{4-}$. Finally, the magnetic susceptibility was measured and found to be approximately 0.45 μ_B. A value of ≈1.8 μ_B for a d^1 state is to be expected. Our interpretation of the UV/Vis, ESR and magnetic susceptibility spectroscopic data is that upon addition of $Sb(OAc)_3$ to the lacunary species there is no electron transfer from Sb^{III} to Mo^{VI} with formation of Sb^{IV} or Sb^{V} and one or more Mo^{V} centers; rather, there is only partial electron delocalization with some formation of Mo^{V}.[51] Complete transfer of one electron and localization of an electron at a molybdenum center, i.e. formation (formally) of $[PSb^{IV}Mo^{V}Mo^{VI}_{10}O_{39}]^{4-}$, should have yielded both more intense UV/Vis and ESR spectra, and a magnetic susceptibility for a d^1 state of ≈1.8 μ_B. Since Sb^{IV} is an uncommon oxidation state, a transfer of two electrons could be contemplated to form $[PSb^{V}Mo^{V}_{2}Mo^{VI}_{9}O_{39}]^{4-}$; this, however, should have yielded a yet more intense absorbance at 750 nm and no or a weak ESR signal due to antiferromagnetic coupling.

Oxidation of $[Q_4PSb^{III}(H_2O)Mo_{11}O_{39}]$

The Sb^{III}-substituted polyoxomolybdate can conveniently be oxidized to a Sb^{V} analog by either molecular bromine or ozone. Addition of one equivalent of Br_2 to $[Q_4PSb^{III}(H_2O)Mo_{11}O_{39}]$ immediately forms a yellow compound. Similarly, bubbling ozone though a CH_3CN solution of $[Q_4PSb^{III}(H_2O)Mo_{11}O_{39}]$ for five minutes also yielded a yellow solution with a slight greenish tint. Both treatments gave ESR-silent compounds and appeared to be diamagnetic from the magnetic susceptibility measurements, suggesting that all the Sb^{III} atoms were oxidized to Sb^{V}. The IR spectra of the products resulting from the two treatments were somewhat different. The oxidation with bromine gave a compound whose IR spectrum (Figure 2d) was essentially unchanged from that of the original Sb^{III} compound(Figure 2b). On the other hand, treatment with ozone gave a product whose IR spectrum was slightly different (Figure 2c). Most notable is the split peak at 951 and 939 cm^{-1}. The ^{31}P NMR spectra of the two compounds are also different: treatment with Br_2 gave a compound with a peak at $\delta = -5.00$, whereas with ozone a peak at $\delta = -5.25$ was obtained. As will be discussed below, the resulting Sb^{V}-containing compounds can also be differentiated based on their activity in the stoichiometric oxidation of alcohols (Table 2). Based on the IR spectra and elementary analysis, we assume that oxidation by bromine yielded $[Q_3PSb^{V}(Br)Mo_{11}O_{39}]$while with ozone $[Q_4PSb^{V}(O)Mo_{11}O_{39}]$was obtained according to the reaction pathways in Equation (2) and Equation (3).

$$Q_4PSb^{III}Mo_{11}O_{39} + Br_2 \longrightarrow Q_3PSb^{V}(Br)Mo_{11}O_{33} + QBr$$

$$Q_4PSb^{III}Mo_{11}O_{39} + O_3 \longrightarrow Q_4PSb^{V}(O)Mo_{11}O_{39} + O_2$$

The appearance of an additional peak in the IR spectra of $[Q_4PSb^{V}(O)Mo_{11}O_{39}]$ at 939 cm^{-1} is most likely explained by the $Sb = O_t$ vibration — a Sb−Br absorption would be expected at lower out-of-range energies (<400 cm^{-1}).

Anaerobic and Catalytic Aerobic Oxidation of Alcohols by Sb-POM

In Table 2 we have summarized the results for the anaerobic oxidation (under argon) of various alcohols by phosphoantimonato(V)molybdates in benzonitrile at 135 °C: primary alcohols are oxidized selectively to aldehydes and secondary alcohols to the corresponding ketones. From these results it is easy to determine that $[Q_4PSb^{V}(O)Mo_{11}O_{39}]$ is a more active oxidant than $[Q_3PSb^{V}(Br)Mo_{11}O_{39}]$. The order of activity is benzylic > allylic ≈ cycloaliphatic > secondary aliphatic > primary aliphatic alcohols. These results indicate that the C−H bond strength determines the reactivity of the alcohol. During the reaction the yellow color of $[Q_4PSb^{V}(O)Mo_{11}O_{39}]$ and $[Q_3PSb^{V}(Br)Mo_{11}O_{39}]$ was changed to the deep-green color of a reduced polyoxometalate. The reaction stoichiometry and the extinction coefficient measured at 750 nm indicate that a two-electron-reduced polyoxometalate was formed.

Aerobic catalytic oxidation of alcohols and other substrates by $[Q_4PSb^{V}(O)Mo_{11}O_{39}]$ as catalyst was also invest-

Table 2. Anaerobic oxidation of alcohols by phosphoantimonato(V) molybdates

Substrate	Product	Yield of polyoxometalate[a]	
		$[Sb(O)PMo_{11}O_{39}]^{4-}$	$[SbBrPMo_{11}O_{39}]^{3-}$
Benzyl alcohol	benzaldehyde	100 (100)[b]	100 (80)[b]
1-Phenylethanol	acetophenone	100	100
Cinnamyl alcohol	cinnamaldehyde	100	100
1-Hexanol	1-hexanal	70	0
2-Hexanol	2-hexanone	98	50
Cyclohexanol	cyclohexanonone	100 (38)[b]	85 (0)[b]
cis-2-Hexanol	*cis*-2-hexanal	100	45
trans-2-Hexanol	*trans*-2-hexanal	100	40
cis-3-Hexanol	*cis*-3-hexanal	80	15

[a] Reaction conditions: alcohol (40 mM) and polyoxometalate (5 mM) were treated with 1 mL of PhCN at 135 °C under Ar for 20 h. − [b] In acetonitrile at 80 °C.

Table 3. Aerobic oxidation catalyzed by $[Q_4PSb^{V}(O)Mo_{11}O_{39}]$

Substrate	Product	Conversion, mol-%[a]
Benzyl alcohol	benzaldehyde	76 (5)[b]
1-Phenylethanol	acetophenone	80 (9)[c]
Cinnamyl alcohol	cinnamaldehyde	100
4-Methoxybenzyl alcohol	4-methoxybenzaldehyde	62
4-Methylbenzyl alcohol	4-methylbenzaldehyde	78
4-Nitrobenzyl alcohol	4-nitrobenzaldehyde	100 (62)[d]
Benzylamine	$PhCH_2N=CHPh$	40
Dihydroanthracene	anthracene	7 (62)[c]

[a] Reaction conditions: substrate (100 mM) and $[Q_4PSb^{V}(O)Mo_{11}O_{39}]$ (1 mM) were reacted in 1 mL of PhCN at 135 °C under 2 atm. O_2 for 20 h. − [b] Catalyst: $Q_4PSb^{III}(H_2O)Mo_{11}O_{39}$. − [c] Catalyst: $Q_5PV_2Mo_{10}O_{40}$. − [d] 4-Nitrobenzyl alcohol, 300 mM.

igated (Table 3) in pressure tubes at 135 °C under two atmospheres of oxygen with PhCN as solvent. Of the alcohols tested only benzylic alcohols were oxidized in appreciable yields. Cyclohexanol, 2-hexanol, and *cis*-2-hexenol all gave less than 5 mol-% conversion in this catalytic system with $[Q_4Sb(O)PMo_{11}O_{39}]$ as catalyst. Interestingly, the electron-donating methoxy substituent reduced the yield whereas the electron-withdrawing nitro substituent increased the yield significantly (up to 186 turnovers were measured). It is notable that benzoic acids as overoxidation products were not detected under the reaction conditions. Benzylamine was also oxidatively dehydrogenated to the corresponding Schiff base imine, $PhCH=NCH_2Ph$, in a reaction that has been observed in the past for $[PV_2Mo_{10}O_{40}]^{5-}$. In fact, the use of the better known oxidation catalyst $[Q_5PV_2Mo_{10}O_{40}]$ gave an activity about one order of magnitude less than for the oxidation of benzylic alcohols. On the other hand, in the oxydehydrogenation of dihydroanthracene to anthracene, $[Q_4PSb^{V}(O)Mo_{11}O_{39}]$ was significantly less active than $[Q_5PV_2Mo_{10}O_{40}]$ (7 mol-% conversion vs. 65 mol-%). Also interesting is to note that the antimony(III) compound $[Q_4PSb^{III}(H_2O)Mo_{11}O_{39}]$ showed little catalytic activity. Finally, in a competitive oxidation of benzyl alcohol and [D7]benzyl alcohol a kinetic isotope effect of 2.8 ± 0.1 was measured. It would be premature and presumptuous to present a mechanistic pathway for oxydehydrogenation catalyzed by $[Q_4PSb^{V}(O)Mo_{11}O_{39}]$. However, the low kinetic isotope effect, the higher activity of 4-nitrobenzyl alcohol vs. 4-methoxybenzyl alcohol and the relative inactivity compared to $[Q_5PV_2Mo_{10}O_{40}]$ for dihydroanthracene oxidation, where mechanistic research has indicated an electron-transfer-initiated process,[33−34] all indicate that for $[Q_4PSb^{V}(O)Mo_{11}O_{39}]$ a different mechanism is to be expected.

Experimental Section

Synthesis of $Q_4PSb^{III}(H_2O)Mo_{11}O_{39}$: $[Q_4H_3PMo_{11}O_{39}]$ (Q^+ = tetra-*n*-butylammonium cation) was prepared by the literature procedure,[43] and its purity ≈99% was determined by ^{31}P NMR, infrared and UV/Visible spectroscopic analysis. $[Q_4PSb^{III}(H_2O)Mo_{11}O_{39}]$ was synthesized as follows: antimony(III) acetate (0.116 g, 0.39 mmol, 1.5 equiv.) was added to a solution of $Q_4H_3PMo_{11}O_{39}$ (0.7 g, 0.26 mmol) in acetonitrile (30 mL). The color slowly changed from yellow-green to deep-green. After 2 hours of stirring the reaction mixture was filtered. The solution was placed in a crystallizing dish and allowed to evaporate slowly at room temperature. The crude, deep green crystalline product was separated by filtration and recrystallized from acetonitrile to give green crystals of $[Q_4PSb^{III}(H_2O)Mo_{11}O_{39}]$ (0.6 g, 84%). $C_{64}H_{146}Mo_{11}N_6O_{40}PSb$ (2819.91): calcd. C 27.26, H 5.15, N 1.99; found C 27.45, H 5.36, N 1.72. ICP-MS ratio P:Sb:Mo = 1:1:11. The UV/Vis spectrum was measured on an HP 8452 diode array instrument. − λ_{max} (CH_3CN) = 218 nm (ε = 830 mM^{-1} cm^{-1}), 316 (ε = 18), 750 (ε = 0.17). The ^{31}P NMR was measured on a Bruker DPX 250 spectrometer at 101.254 MHz with H_3PO_4 as external standard, a single peak at δ = −1.20 was observed. The IR spectrum was measured on a Nicolet Protégé 460 with a sample deposited on a KBr disk by evaporation of an CH_3CN solution. Peaks at $\tilde{\nu}$ = 1061, 955, 862, 802 cm^{-1} were observed. Cyclic voltammetry was measured on a BAS −1 instrument fitted with a glass carbon working electrode. A 0.5 mM solution of $[Q_4PSb^{III}(H_2O)Mo_{11}O_{39}]$ in acetonitrile with 1 M QBF_4 was used for the measurements. $E_{1/2}$ = −0.14, +0.2 and an irreversible anodic wave at +0.9 V vs. SCE (similar to $Q_3PMo_{12}O_{40}$). The ESR spectra were measured at room temperature on a Bruker ER-200 spectrometer with DPPH as reference. The spectrum of 1 mM $[Q_4PSb^{III}(H_2O)Mo_{11}O_{39}]$ in CH_3CN at 25 °C showed a weak isotropic signal at $g = 1.937$, width 75 G. The average magnetic susceptibility was measured on a Sherwood Scientific Magnetic Susceptibility Balance as a neat powder at 22 °C. Pascal's constants were used to obtain the final diamagnetic correction. To avoid errors in our estimates of the diamagnetic correction the susceptibility of the lacunary $[Q_4H_3PMo_{11}O_{39}]$ was measured as reference. The difference between the magnetic susceptibility of $[Q_4H_3PMo_{11}O_{39}]$ and $[Q_4H_3PMo_{11}O_{39}]$ allowed us to calculate the effective magnetic moment of the delocalized blue electron[52] which was 0.45 μ_B. Slow concentration of the acetonitrile solution gave emerald-green prisms which were used for the single-crystal X-ray diffraction investigation.

Crystal Structure Determination of $[Q_4PSb^{III}(H_2O)Mo_{11}O_{39}]$: Data were collected on dark-green prisms 0.2 × 0.2 × 0.1 mm using a Nonius−Kappa CCD diffractometer with Mo-K_α ($\lambda = 0.71073$ Å) radiation. 43215 reflections and 10857 independent reflections were collected with $-40 \leq h \leq 39$, $0 \leq k \leq 12$, $-23 \leq l \leq 24$, frame scan width of 1.0°, scan speed 1° per 20 sec and a typical mosaicity of 0.5°. Data were processed with Denzo−Scalepack.[53] The crystallographic data are presented in Table 1. The structure was solved by Patterson methods with SHELXS-97. Full-matrix least-squares refinement was based on F^2 with SHELX-97. Refinement proceeded to convergence by minimizing $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. 1229 parameters with 580 restraints yielded a final $R = 0.0651$ for data with $I > 2\sigma(I)$ and $R = 0.0673$ for all 10857 reflections. A final difference-Fourier synthesis map showed several peaks less than 2.008 e/Å^3 scattered about the unit cell without significant features. The goodness-of-fit on F^2 was 1.062. As is common for these polyoxometalate structures the counter cations were mostly disordered and therefore also incomplete but are equally distributed throughout the cell.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149090. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Oxidation of $[Q_4PSb^{III}(H_2O)Mo_{11}O_{39}]$: A solution of $[Q_4PSb^V(O)Mo_{11}O_{39}]$ was prepared by bubbling an oxygen stream (250 mL/min) containing 9 μg/mL of ozone through a 1.6 mM solution of $[Q_4PSb^{III}(H_2O)Mo_{11}O_{39}]$ in acetonitrile. After 5 min the color changed from green to yellow. UV (CH_3CN): $\lambda_{max} = 218$ nm, 302 (sh). − ^{31}P NMR: $\delta = -5.25$. − IR: $\tilde{\nu} = 1059$, 951, 939, 881 and 804 cm^{-1}. A solution of $[Q_3PSb^V(Br)Mo_{11}O_{39}]$ was prepared by addition of one equivalent Br_2 as a 0.4 mM solution of Br_2 in acetonitrile to a 1.6 mM solution of $[Q_4PSb^{III}(H_2O)Mo_{11}O_{39}]$ in acetonitrile. The color immediately changed from green to yellow. UV: $\lambda_{max} = 270$ nm. − ^{31}P NMR: $\delta = -5.00$. − IR: $\tilde{\nu} = 1061$, 954, 879 and 802 cm^{-1}.

Oxidation Reactions with Phosphoantimonato(V) Molybdates: Typically, oxidation reactions were carried out in 13 mL glass pressure tubes by loading the vial with the appropriate amounts of substrate, polyoxometalate and solvent. The tube was purged and loaded with the desired gas (argon or oxygen) by using three freeze, pump and thaw cycles. The reaction tube was placed in a thermostated oil bath and the mixture stirred magnetically. Aliquots were removed at the appropriate time intervals for analysis by gas chromatography. Oxidation reaction products were characterized using reference compounds, when available, by use of GLC (HP-6890 gas chromatograph) with a flame ionization detector and a 15 m × 0.32 mm 5% phenylmethylsilicone (0.25 μm coating) capillary column and helium carrier gas. Products whose initial identity was questionable were unambiguously identified using a gas chromatograph equipped with a mass-selective detector (GC-MS HP 5973) equipped with the same column.

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