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$[Ag_6(PMo_{10}V_2O_{40})](CH_3COO)\cdot 8H_2O$: A 3D Macrocationic Polyoxometallic Keggin Complex

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Silver atoms and strongly interlinking Keggin units ensure the tridimensionnal macrocationic structure of $[Ag_6(PMo_{10}V_2O_{40})](CH_3COO)\cdot 8H_2O$, which catalyzes O_2-based oxidation of *p*-methoxytoluene in acetic acid by air.

The development of new catalysts for selective oxidation by dioxygen presents a great importance both in economic plans and in fundamental studies. Heteropolyoxomolybdates, particularly the Keggin vanadomolybdophosphates $[PMo_{12-x}V_xO_{40}]^{(3+x)-}$ (with $x = 1-3$), have been widely used as homogeneous and heterogeneous catalysts for the oxidation of numerous organic molecules such as alcohols, aldehydes, isobutyric acid, or alkanes. The content of V, the nature of the counterions, and the solid state structure could modify their acidic and oxidizing proprieties and their stability.[1]

Recently, the structure of $Ag_{10.4}P_2V_4Mo_{20}O_{80}\,(NO_3)_{0.4}(CH_3CN)_{17.3}(H_2O)_{1.5}$ and its catalytic properties in selective O_2 sulfoxidation of 2-chloroethyl ethyl sulfide have been reported by J. T. Rhule et al.[2] A probable synergistic effect between the Ag(I) counterions and the redox active V(V) centers inside the Keggin anion has been postulated.

In the present work, we report the preparation, structure, and catalytic activity of $[Ag_6(PMo_{10}V_2O_{40})](CH_3COO)\cdot 8H_2O$ for the oxidation of *p*-methoxytoluene by air compared with that of $H_5[PMo_{10}V_2O_{40}]$.

The heteropolyacid $H_5[PMo_{10}V_2O_{40}]\cdot 23H_2O$ (named HPV2) was synthesized according to the literature,[3] except the crystallization was realized at 4 °C. The sample obtained was characterized by IR, TG, and elemental analysis. $[Ag_6(PMo_{10}V_2O_{40})](CH_3COO)\cdot 8H_2O$ crystals were obtained at room temperature from an aqueous solution containing silver acetate and $H_5[PMo_{10}V_2O_{40}]$.[4]

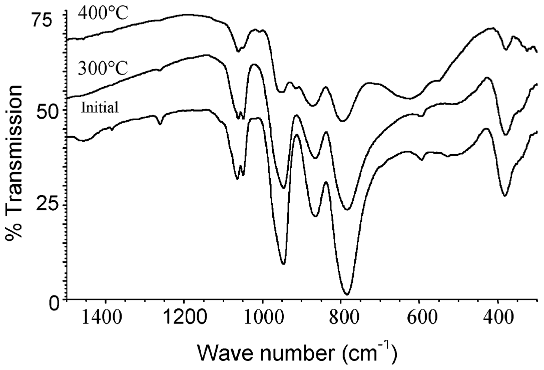

Figure 1. IR spectra of $[Ag_6(PMo_{10}V_2O_{40})](CH_3COO)\cdot 8H_2O$: initial and heated samples under air flow at 300 and 400 °C.

The Keggin structure in the $[Ag_6(PMo_{10}V_2O_{40})](CH_3COO)\cdot 8H_2O$ crystals was confirmed by IR spectroscopy. The IR spectrum (Figure 1) shows intense bands at 1064, 946, 864 cm^{-1}, a broad band at 785 cm^{-1}, characteristic of the Keggin structure,[5] and one additional shoulder at 1050 cm^{-1} due to the partial replacement of Mo by V in the Keggin structure. A large weak band at 1457 cm^{-1} was attributed to the $\nu_a(COO^-)$ stretching vibration of acetate.[6]

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(4) An 5 g portion of $H_5[PMo_{10}V_2O_{40}]\cdot 23H_2O$ was first dissolved in 10 mL of water, and then 2.4 g of solid CH_3COOAg was added very slowly. The precipitate formed was filtered and dried (named: AgPV2) and used for a catalytic test. The filtrate was kept for crystallization at room temperature. The small red stable crystals obtained were shaped like sea urchins with pretty fine needles. Crystals were also grown from acetonitrile solution. Analysis of crystals, % found (calcd.): Ag 24.95 (25.14), Mo 37.85 (37.27), V 4.01 (3.96), P 1.21 (1.20), H 0.72 (0.74).

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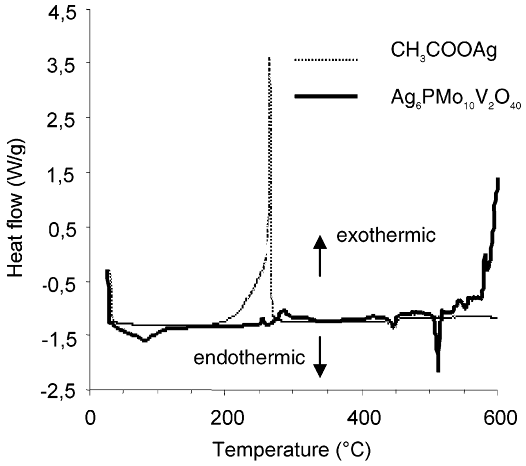

Figure 2. DSC curves (3 mg) of $[Ag_6(PMo_{10}V_2O_{40})](CH_3COO)·8H_2O$ and CH_3COOAg under O_2 flow (peak at 450 °C resulted from the DSC apparatus).

Elemental analysis gave the atomic ratios Ag/P, Mo/P, and V/P equal to 5.90, 10.11, and 2.02, respectively,[4] in agreement with the chemical formula "$Ag_6PMo_{10}V_2O_{40}$", determined by X-ray diffraction.

Five Ag(I) ions are expected to balance the five negative charges of $[PMo_{10}V_2O_{40}]^{5-}$, but six Ag(I) ions were found by XRD and chemical analysis per Keggin unit. Two possibilities exist to ensure the electric balance: Keggin anion is reduced to $[PMo_{10}V_2O_{40}]^{6-}$, or an acetate anion is present in the lattice. The crystal sample was obtained in aqueous solution under air atmosphere, and no reducing agent is present in solution. Furthermore, the crystals are red translucent, not blue as usually observed for reduced Keggin anions $[PMo_{12-x}V_xO_{40}]^{(3+x)-}$ (with $x = 0-3$). So, one can assume that Keggin anions are not reduced. On the other hand, the IR spectrum shows a weak and large band at 1457 cm^{-1}, attributed to the CO_2^- stretching vibration that would confirm the presence of acetate in the lattice. DSC experiments performed under O_2 flow (Figure 2) show one small exothermal peak at 255 °C corresponding to the combustion of acetate. IR, DSC, elemental analysis, and XRD led us to attribute to the compound the following chemical formula: $[Ag_6(PMo_{10}V_2O_{40})](CH_3COO)·8H_2O$. This formula agrees also with the TG data showing a weight loss of 6.83% from 20 to 600 °C.

The structure of $[Ag_6(PMo_{10}V_2O_{40})]^+$ determined by X-ray diffraction[7] is that of a three-dimensional macrocation. All the Keggin units are interlinked by Ag(I) in a 3D arrangement through O−Ag−O bridging bonds. All the Ag(I) ions are engaged in the three-dimensional junctions. Four types of silver positions Ag1, Ag2, Ag3, and Ag4 are distinguished. As shown in Figure 3, Ag1 is coordinated to eight oxygen atoms of two Keggin units, ensuring a one-dimensional linkup between the Keggin units. The construction of the three-dimensional structure is ensured by Ag2, Ag3, and Ag4.

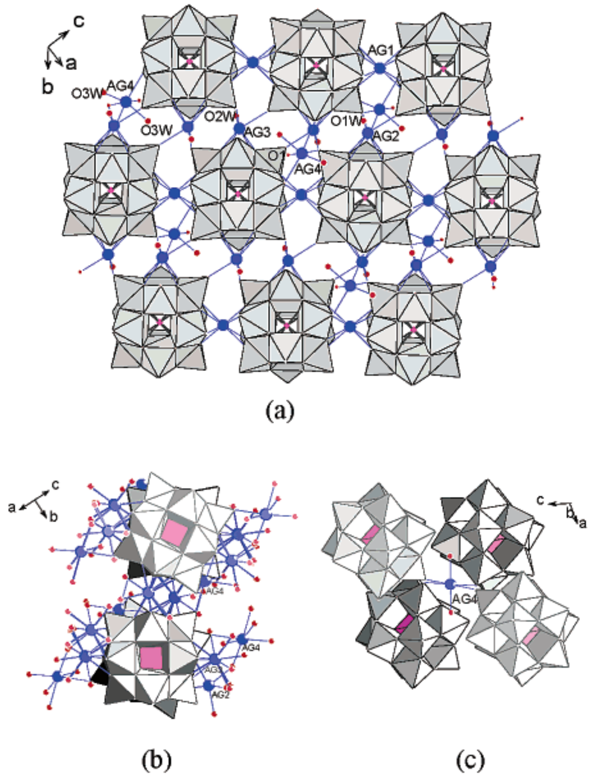

Figure 3. Three-dimensional structure of $[Ag_6(PMo_{10}V_2O_{40})]^+$: (a) view of the connection of the Keggin units by silver atoms in plane (−1, 1, 1). (b) Profile view of part (a) in addition to the silver atoms out of the plane of Keggin units. (c) Coordination of Ag4 to four Keggin units and two water molecules.

Both Ag2 and Ag3 are seven-coordinated: one water molecule, four oxygen atoms of one Keggin unit, and two oxygen atoms of two different Keggin units. Ag4 links four oxygen atoms of four noncoplanar Keggin units and two water molecules (Figure 3c).

It must be noted that all the silver atoms are ligated to at least two different Keggin units. The Ag−O$_k$ (O$_k$, oxygen atoms of Keggin units) bond lengths vary from 2.466 to 2.779 Å and are in the same order as that obtained in $C_8H_{24}Ag_2Mo_{10}N_2O_{36}.(C_{16}H_{36}N)_4$,[8] $Ag_3Br_4MoOS_3.(C_{16}H_{36}N)_3$,[9] $Ag_2[Mo_{12}O_{46}(AsC_6H_4\text{-}4\text{-}NH_2)_2(AsC_6H_4\text{-}4\text{-}NH_3^+)_2]·(CH_3CN)_8(H_2O)_2$,[10] and $Ag_{10.4}P_2V_4Mo_{20}O_{80}(NO_3)_{0.4}·(CH_3CN)_{17.3}(H_2O)_{1.5}$.[2] They correspond to strong interactions between Ag and oxygen atoms of the Keggin units.

In the Keggin structure, polyhedra share edges and corners, but in Figure 3, all the polyhedra seem to be linked only by edges. In fact, this illusion corresponds to the averaged position of the Keggin units disordered over two positions: the Keggin units are rotated by 90° about the S_4 axis from one to another as compared to the initial Keggin unit. Such a Keggin unit disorder has been reported[11−13] and sometimes named "reverse Keggin" structure.

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(7) $[Ag_6(PMo_{10}V_2O_{40})](CH_3COO)·8H_2O$: monoclinic, $C2/c$ with a = 16.0157(4) Å, b = 14.5507(4) Å, c = 18.0452(4) Å, β = 109.219(1)°, Z = 4, V = 3970.88(17) Å^3, D_{calcd} = 4.248 g·cm^{-3}, T = 293(2) K, λ = 0.71073 Å, μ = 6.547 mm^{-1}. The final statistics based on F^2 are GOF 1.043, R1 = 0.0673, and wR2 = 0.1773 for $I > 2\sigma(I)$. Additional details are available as Supporting Information.

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The structure of $[Ag_6(PMo_{10}V_2O_{40})](CH_3COO)\cdot 8H_2O$ described in this work is totally different from that of $Ag_{10.4}P_2V_4Mo_{20}O_{80}(NO_3)_{0.4}(CH_3CN)_{17.3}(H_2O)_{1.5}$ reported by J. T. Rhule et al.[2] in which the dimer $[Ag_6(PMo_{10}V_2O_{40})_2(CH_3CN)_{10}]^{4-}$ was formed, and two $[PMo_{10}V_2O_{40}]^{5-}$ Keggin anions are linked by two Ag(I) in addition of two nonbridging Ag(I) for each Keggin anion. The two bridging silver atoms coordinate to three terminal oxygen atoms of two Keggin units and one acetonitrile molecule while the four nonbridging Ag(I) ions coordinate to two terminal oxygen atoms of the same Keggin unit and two CH_3CN molecules. More than $^4/_{10}$ of Ag(I) ions are not bonded to any Keggin anion; all Ag(I) centers are four-coordinate. This dimer has been reported to be stable up to 830 °C.

DSC measurements under O_2 flow (Figure 2) of the title $[Ag_6(PMo_{10}V_2O_{40})](CH_3COO)\cdot 8H_2O$ show two small exothermic peaks, respectively, at 255 and 290 °C and one intense endothermic peak at 515 °C. As we have mentioned previously in this paper, the exothermal peak at 255 °C corresponds to the combustion of acetate. Consequently, $^1/_6$ of Ag^+ ions should be present as oxide Ag_2O after the decomposition of acetate. IR spectra (Figure 1) show that the Keggin anion structure is maintained up to 300 °C and a partial decomposition starts at 350 °C. A large band near 640 cm^{-1}, characteristic of the formation of MoO_3, is observed at 350 °C, and its intensity increases from 350 to 400 °C. But no peaks corresponding to the crystalline α-MoO_3 or β-MoO_3 are detected by X-ray thermodiffraction[14] performed under static air atmosphere from 30 to 610 °C. Attempts to identify the new phases formed between 310 and 550 °C were not successful. These phases disappear completely, and no XRD peak is observed above 570 °C. The presence of one intense endothermic peak at 515 °C (under O_2 flux) and the absence of any XRD peak above 570 °C (under static air atmosphere) suggest a breaking of the solid state structure accompanied by the melting of the sample in this range of temperature. For comparison, silver molybdate Ag_2MoO_4 has a melting point of 483 °C.[15]

Table 1. Catalytic Reactivity in *p*-Methoxytoluene Oxidation by Air[a]

catalyst	conv (%)	sel[b] (%)	yield[c] (%)
HPV2	97.9	4.4	4.3
AgPV2[d]	30.0	38.0	11.4
without catalyst	<2	ND	ND

[a] The catalytic reaction was carried out at 140 °C under initial air pressure of 60 bar, over 3 h, with 2% (mol) of catalyst and 10% (weight) of substrate in CH_3COOH. Analysis by GC using internal standard. [b] Selectivity is referred to the following products: 4-methoxybenzyl alcohol, 4-methoxybenzaldehyde, 4-methoxybenzoic acid, and 4-methoxybenzyl acetate. [c] Yield (%) = conv (%) × sel (%). [d] Silver salt was not soluble in the above reaction conditions; its initial B. E. T. surface area was 12 $m^2\cdot g^{-1}$.

The powder sample AgPV2 obtained by precipitation was used for a preliminary study of the catalytic reactivity in oxidation of *p*-methoxytoluene by air. As compared with $H_5[PMo_{10}V_2O_{40}]\cdot 23H_2O$ (named HPV2), the first results are rather promising and are given in Table 1.

The replacement of the counterions H^+ by Ag(I) increases noticeably the yield to oxidation products from 4.3% to 11.4%. This increase in yield is due to an enhancement in selectivity despite a decrease in conversion. Certainly, Ag(I) plays a determining role in this enhancement. In order to understand it, further studies with samples containing both H^+ and Ag(I) as counterions ions will be realized.

To our knowledge, the structure of $[Ag_6(PMo_{10}V_2O_{40})]^+$ reported in this work is the first tridimensional macrocationic structure of polyoxometallic Keggin complexes, in which the silver atoms strongly interbond the Keggin units. The preliminary promising results obtained in oxidation of *p*-methoxytoluene by air demonstrate that this silver salt can catalyze air oxidation of alkanes, with strongly improved selectivity when compared to the protonated analogue.

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Supporting Information Available: Crystallographic information in CIF format. Patterns of X-ray thermodiffraction (XRTD) performed under the static air atmosphere and view of the unit cell. This material is available free of charge via the Internet at http://pubs.acs.org.

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