Inorg. Chem. **1996,** *35,* 2403−2405 **2403**

A Bivanadyl Capped, Highly Reduced Keggin Polyanion, $[PMo^{V}_{6}Mo^{VI}_{6}O_{40}(V^{IV}O)_2]^{5-}$

Qin Chen and Craig L. Hill*

Department of Chemistry, Emory University,
Atlanta, Georgia 30322

Received September 20, 1995

Introduction

Polyoxometalates containing Keggin[1] moieties are of fundamental and practical interest. They are capable of being fine-tuned at the molecular level to promote a variety of applications ranging from environmentally benign catalysis to medicine.[2−6] In contrast to a large number of literature Keggin and transition-metal-substituted Keggin species, only four capped Keggin derivatives are structurally known.[7] In context with our ongoing research in oxidatively resistant clusters and homogeneous catalytic oxidation,[8] we have exploited hydrothermal techniques to develop new Keggin derivatives which could facilitate processes that are compatible with environmentally friendly conditions and operations, such as wood pulp bleaching technology.[9,10] We report here the hydrothermal synthesis, spectroscopic characterization, X-ray crystal structure, and evaluation of the kinetic stability of $(Et_3NH)_5[PMo^{V}_6Mo^{VI}_6O_{40}(V^{IV}O)_2]$, (TEA) **1**, a bicapped, highly reduced vanadylpolymolybdophosphate Keggin complex.

Experimental Section

General Materials and Methods. All chemicals were commercially available reagent grade. Deionized water was used for all syntheses and studies (spectroscopic characterization and kinetics). Where appropriate, Schlenk line techniques were used. Elemental analyses for all elements except oxygen (calculated by difference) were conducted at E + R Microanalytical Laboratory, Inc. (Corona, NY). Infrared spectra were obtained for KBr pellets with 2−5% wt of the sample using a Nicolet 510 FTIR spectrophotometer. The electronic adsorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer equipped with a temperature controller. ^{31}P and ^{51}V NMR spectra were recorded using a IBM WP-200SY NMR spectrometer at 81.01 and 52.58 MHz and were referenced to 85% H_3PO_4 and 100% $VOCl_3$, respectively. Solution pH measurements were made using a Model 240 Corning pH meter. Cyclic voltammograms were obtained in H_2O with the NaCl as the supporting electrolyte using a Princeton Applied Research Model 173 potentiostat/galvanostat system. (Glassy carbon, Ag/AgCl, and Pt wire were the working, reference, and auxiliary electrodes, respectively.) Redox titrations[11] were carried out with $Ce^{IV}NO_3 \cdot 6H_2O$ in H_2O under anaerobic conditions. Kinetic stabilities were evaluated by following the characteristic electronic absorption maxima of the complex (λ = 708 nm) at 25.0 ± 0.1 °C. Integrated rate laws[12] were applied to the experimental data using KaleidaGraph[13] (see plot in Supporting Information).

Table 1. Crystallographic Data for (TEA) **1**

formula	$C_{30}H_{80}Mo_{12}N_5O_{42}PV_2$	ρ_{calcd}, Mg m^{-3}	2.427
fw	2467.12	μ, mm^{-1}	2.527
cryst syst	triclinic	temp, K	173
space group	*P*1 (No. 1)	radiation (λ, Å)	0.710 73
a, Å	14.138(3)	θ range, deg	1.0−22.5
b, Å	14.301(3)	scan speed (ω), deg/min	5−60
c, Å	16.816(3)	no. of reflcns	10100
α, deg	95.71(3)	no. of restraints	3
β, deg	92.25(3)	no. of params	878
γ, deg	92.56(3)	$R_1[I > 2\sigma(I)]^a$	0.0802
V, Å^3	3376.5(12)	wR_2^b	0.2133
Z	2	GOF	1.075

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w((F_o^2)^2]\}^{1/2}$.

Synthesis of (TEA) 1. Sodium molybdate(VI) dihydrate (0.968 g), 0.184 g of vanadyl(IV) sulfate trihydrate, 0.12 mL of 85% orthophosphoric acid, 0.275 g of triethylammonium hydrochloride, and 7.0 mL of deionized water were mixed (the mole ratio of $Na_2MoO_4 \cdot 2H_2O$, $VOSO_4 \cdot 3H_2O$, H_3PO_4, $(C_2H_5)_3N \cdot HCl$, and H_2O: 10:2:5:5:970) and heated at 180 °C and autogenous pressure for 72 h in a 23-mL Teflon-lined Parr acid digestion bomb. After being cooled to room temperature, the bomb was allowed to stand for 4−10 days, during which deep blue-black block crystals of $[(C_2H_5)_3NH]_5[PMo^{V}_6Mo^{VI}_6O_{40}(V^{IV}O)_2]$, (TEA) **1**, formed in the deep blue solution. The crystalline materials were filtered, washed with dry acetone, and vacuum dried to give about 30% yield (based on Mo). Upon standing in the air, the shiny crystals became opaque very quickly. Anal. Calcd for **1**, $C_{30}H_{80}Mo_{12}N_5O_{42}PV_2$: C, 14.61; H, 3.27; Mo, 46.67; N, 2.84; O, 27.24; P, 1.26; V, 4.13. Found: C, 15.05; H, 3.38; Mo, 46.42; N, 2.89; O, 26.94 (by difference); P, 1.32; V, 4.00. IR (KBr pellet, cm^{-1}): 3417 (m), 2969 (m), 1460 (m), 1396 (w), 1260 (m), 1090 (w), 1061 (w), 1026 (m), 947.8 (vs), 869.5 (w), 791.2 (vs), 705.8 (m), 648.9 (w). UV−visible [H_2O; λ_{max}, nm (ϵ, cm^{-1} M^{-1})]: 214 (5.0×10^4), 308 (1.7×10^4) (sh), 708 (1.4×10^3).

Crystallography. A fresh deep blue-black crystal (0.40 × 0.20 × 0.50 mm) taken from the mother liquid of a reaction vessel was mounted on a glass fiber and centered at −100 °C on a Siemens P4 four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). A total of 10 100 reflections ($2\theta_{max}$ = 45°) were collected using ω scan mode, of which 10 086 were unique. Details of crystal data, measurements of intensities, and data processing are summarized in Table 1. The structure was solved by direct methods[14] and refined by full-matrix-least-square-on-F^2 techniques (8835 reflections with $F^2 > 2\sigma(F_o^2)$),[15] using anisotropic temperature factors for all Mo and V atoms, and isotropic temperature factors for the remaining

---

(1) Brown, G. M.; Noe-Spirlet, M. R; Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1977**, *B33*, 1038. Evans, H. T., Jr. *Perspect. Struct. Chem.* **1971**, *4*, 1.

(2) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983.

(3) Day, V. W.; Klemperer, W. G. *Science (Washington, D.C.)* **1985**, *228*, 533.

(4) Pope, M. T.; Muller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34.

(5) Pope, M. T.; Muller, A. *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994.

(6) Hill, C. L.; Prosser-McCartha, C. M. *Coord. Chem. Rev.* **1995**, *143*, 407.

(7) See the following examples. In polyoxovanadium chemistry: $V_{15}O_{42}^{9-}$, Hou, D.; Hagen, K. S.; Hill, C. L. *J. Chem. Soc., Chem Commun.* **1993**, 426. In polyoxovanadium phosphate chemistry: $[PV_{14}O_{42}]^{9-}$, Kato, R.; Kobayaski, A.; Sasaki, Y. *J. Am. Chem. Soc.* **1980**, *102*, 6572; $[H_4PV_{14}O_{42}]^{9-}$, Khan, M. I.; Zubieta, J.; Toscano, P. *Inorg. Chim. Acta* **1992**, *193*, 17. In polyoxovanadium/polyoxomolybdenum arsenate chemistry: $[H_4As_3Mo_{12}O_{40}]^{-}$, Khan, M. I.; Chen, Q.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 2924; $[H_{12}As_3V_{12}O_{42}]^{3-}$, Khan, M. I.; Chen, Q.; Zubieta, J. *Inorg. Chim. Acta* **1993**, *212*, 199; $[AsV_{14}O_{42}]^{9-}$, Huang, G. Q.; Zhang, S. W.; Wei, Y. G.; Shao, M. C. *Polyhedron* **1993**, *12*, 1483. Also see the unique structure of the bridged and capped Keggin species $[Mo_{16}V_{14}O_{84}]^{7-}$: Zhang, Y.; Haushalter, R. C.; Clearfield, A. *J. Chem. Soc., Chem.. Commun.* **1995**, 1149.

(8) Hou, D.; Hagen, K. S.; Hill, C. L. *J. Am. Chem. Soc.* **1992**, *114*, 5864; Combs-Walker, L. A.; Hill, C. L. *J. Am. Chem. Soc.* **1992**, *114*, 938; Weeks, M. S.; Khenkin, A. M.; Hou, Y. *Am. Chem. Soc., Div. Pet. Chem. Prepr.* **1992**, *37*, 1093.

(9) Hill, C. L.; Duncan, D. C.; Harrup, M. K. *Comments Inorg. Chem.* **1993**, *14*, 367.

(10) Weinstock, I. A.; Atalla, R. H.; Reiner, Moen, R. S. M. A.; Hammel, K. E.; Houtman, C. J.; Hill, C. L. *New J. Chem.*, in press.

(11) Day, R. A., Jr.; Underwood, A. L. *Quantitative Analysis*; Prentice Hall: Englewood Cliffs, NJ, 1991.

(12) Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*; VCH Publishers: New York, 1992.

(13) Abelbeck Software. *KaleidaGraph*; PSC Inc.: PA, 1993.

(14) Siemens Crystallographic Research Systems. *SHELXTL PC*; Siemens Analytical X-ray Instruments, Inc.: 1990.

(15) Sheldrick, G. M. *SHELX 93*, *Program for structure refinement*; University of Göttingen: Göttingen, Germany, 1993.

0020-1669/96/1335-2403$12.00/0

atoms. All hydrogen atoms were placed at idealized positions and refined as fixed contributors. Severe disorder in the triethylammonium cations was observed, and no attempts were made to model those cations. At final convergence, $R = 0.0802$ and GOF = 1.075 for 878 parameters.

Results and Discussions

The hydrothermal reaction of $Na_2MoO_4{\cdot}2H_2O$, $VOSO_4{\cdot}3H_2O$, H_3PO_4, $(C_2H_5)_3N{\cdot}HCl$, and H_2O in the mole ratio of 10:2:5:5:970 at 180 °C for 72 h followed by crystallization and separation affords the title polyanion, **1**, in about 30% yield (based on Mo). This product yield can be maintained within the pH range of 6.4−7.0. Below this pH range and at increasing ratio of H_3PO_4 to $Na_2MoO_4{\cdot}2H_2O$, the product yield decreases and hydrothermal reaction conditions produce primarily mixtures of conventional mixed addenda vanadopolymolybdate Keggin species $[H_zMo_{12-x-z}V_xPO_{40}]^{3+x-z}$, **2**.[16] Substituting $Na_2MoO_4{\cdot}2H_2O$ with $Na_2WO_4{\cdot}2H_2O$, under similar hydrothermal reaction conditions, yields mixtures of reduced Keggin species $TEA_3Na_2[PW_{12}O_{40}]{\cdot}xH_2O$, **3**, and an isomeric mixture of $TEA_5[PV_2W_{10}O_{40}]{\cdot}xH_2O$, **4**, ($x$ greater than 10), based on elemental, spectroscopic, and single-crystal X-ray diffraction analyses.

The infrared spectrum of (TEA) **1** (2−5% wt in KBr) exhibits characteristic metal−oxo stretching bands between 1000 and 600 cm^{-1}. The following are the absorption frequencies and, in parentheses, their respective assignments:[17] 947.8 cm^{-1} (overlap of the two terminal oxo stretching fundamentals, $\nu(Mo{=}O_t)$ and $\nu(V{=}O_t)$); 869.5 cm^{-1} ($\nu_{as}(Mo{-}O_b{-}Mo)$ arising from "inter" bridges between corner-sharing Mo octahedra); 791.2 cm^{-1} ($\nu_{as}(Mo{-}O_c{-}Mo)$ arising from "intra" bridges between edge-sharing Mo octahedra); 705.8 and 648.9 cm^{-1} (triply-bridged metal−oxo stretching arising primarily from bridges between corner-sharing V square pyramids and Mo octahedra). The $\nu(P{-}O)$ band at 1026 cm^{-1} is of medium intensity, while bands at 3417, 2969, 1460, 1396, 1260, 1090, and 1062 cm^{-1} indicate the presence of triethylammonium ions. The oxygen-to-metal charge transfer absorption maxima in the UV−visible spectrum occur at 214 and 308 (shoulder) nm, and the characteristic combination d−d and intervalence-charge-transfer absorption maxima is at 708 nm. (TEA) **1** is electrochemically inactive on a glassy carbon electrode.

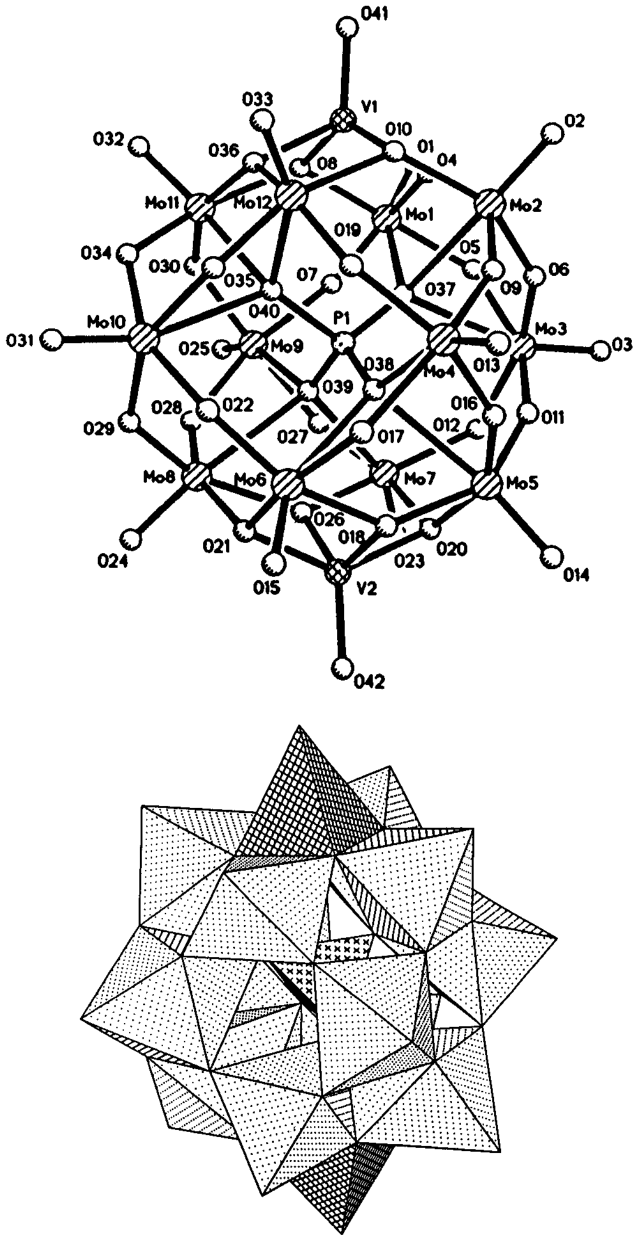

Figure 1. The structure of $[PMo^{V}_6Mo^{VI}_6O_{40}(V^{IV}O)_2]^{5-}$, **1**. Top: the atom-labeling scheme. Selected average bond lengths (Å) and bond angles (deg): $Mo{-}O_t$ 1.66(2), $V{-}O_t$ 1.62(2), $Mo{-}O_b$ 1.89(2), $Mo{-}O_c$ 2.03(3), $V{-}O_c$ 1.93(3), $Mo{-}O_d$ 2.52(2), $P{-}O_d$ 1.54(2); $O_t{-}V{-}O_c$ 115.1(12), $O_d{-}P{-}O_d$ 109.4(13). Abbreviations: O_t = terminal oxo group; O_b = doubly bridging oxo group; O_c = triply bridging oxo group; O_d = quadruply bridging oxo group. Bottom: a polyhedral representation where the Mo octahedra are dotted, the vanadium square pyramids are hatched lines (crossed parallel), and the internal P tetrahedron is covered with small cross symbols.

The X-ray crystal structure determination of (TEA) **1** reveals the presence of triethylammonium cations and discrete molecular anions $[PMo^{V}_6Mo^{VI}_6O_{40}(V^{IV}O)_2]^{5-}$, **1**, shown in Figure 1. The structure of **1** can be best described as an α-Keggin core $\{PMo_{12}O_{40}\}$ with $\{VO\}$ units capping two opposite pits. This bicapped Keggin structure, reminiscent of that of $V_{15}O_{42}^{9-}$ [7] in polyoxovanadium chemistry, exhibits the common Keggin core which consists of four internally edge-shared triads (Mo_3O_{13}) corner-shared to each other and disposed tetrahedrally around a central T_d atom. Caps are formed through the ligation of oxygen atoms on the two opposite $\{Mo_4O_4\}$ faces or pits to each $\{VO\}$ unit such that square pyramidal vanadium coordination environments are generated. Bond length based valence sum calculations[18] establish that the V centers are in the +4 oxidation state, while the Mo centers are in +5/+6 oxidation states. These calculations also indicate that three of the six electrons are primarily localized on three Mo centers (Mo3, Mo9, and Mo11), and the remaining three electrons are primarily delocalized on six Mo centers (Mo2, Mo4, Mo6, Mo7, Mo8, and Mo10). The oxidation state assignments are also consistent with the charge requirement from the anion and the results of redox titration with $Ce^{IV}NO_3{\cdot}6H_2O$ in H_2O under anaerobic conditions. The coupled effect of capping and reduction of the parent Keggin core, lowers the $\bar{4}3m$ symmetry to an idealized D_{2d}.

Compound **1** is fairly stable in water under anaerobic conditions, and, interestingly, decomposes with second-order kinetics ($k_2 = 1.83 \times 10^{-6}$ M^{-1} min^{-1} at 25.0 ± 0.1 °C, 25-point fit with $R = 99.23\%$, Figure S7 in Supporting Information). Under aerobic conditions, however, the decomposition kinetics of **1** are unusually complex exhibiting conventional

---

(16) Other pertinent vanadomolybdophosphate and vanadotungstophosphate Keggin species: Petterssen, L.; Andersson, I.; Selling, A.; Grate, J. H. *Inorg. Chem.* **1994**, *33*, 982; Tsigdinos, G. A.; Hallada, C. J. *Inorg. Chem.* **1968**, *7*, 437; Domaille, P. J.; Watunya, G. *Inorg. Chem.* **1986**, *25*, 1239.

(17) Rocchioccioli-Deltcheff, C. Fournier, M.; Frank, R.; Thouvenot, R. *Inorg. Chem.* **1983**, *22*, 207.

(18) O'Keeffe, M.; Navrotsky, A. *Structure and Bonding in Crystals*; Academic Press: New York, 1981.

kinetics followed by autocatalytic behavior and rendering attempted fits to single integral rate laws inappropriate. Over a period of 20−24 h at 25.0 ± 0.1 °C in water, **1** completely oxidizes and decomposes. The resulting solution has a pH of 3.0 and the ^{51}V NMR spectrum exhibits a single peak at −534 ppm (referenced to neat $VOCl_3$), consistent with the formation VO_2^+ ions.[19] The ^{31}P NMR spectrum of this solution shows a single peak at 3.09 ppm (referenced to 85% H_3PO_4) that is not characteristic of the expected $PMo_{12}O_{40}^{3-}$.[20] Repeated attempts to isolate this species proved to be fruitless. Compound **1** is too reduced to oxidize phenolic lignin model compounds and too slow in its reaction with O_2 to be effective as an autoxidation or mineralization initiator.

In summary, a new and highly reduced polyanion has been prepared using hydrothermal synthesis techniques and thoroughly characterized. It is clear from this structure, and those of other Keggin polyoxometalates of any oxidation state with two vanadium capping units, that this vanadium capping phenomenon is fairly general and is controlled primarily by the charge on the Keggin moiety and the factors that dictate this charge.

Acknowledgment. We thank the National Institutes of Health and the U.S. Army Research Office for support.

Supporting Information Available: Complete listings of crystal data, atomic coordinates and isotropic displacement coefficients, bond lengths and bond angles, anisotropic displacement parameters, and hydrogen coordinates and displacement parameters and a second-order kinetic plot for the decomposition of (TEA) **1** in deionized water under anaerobic conditions (Figure S7) (17 pages). Ordering information is given on any current masthead page.

IC951231N

---

(19) Pope, M. T.; Dale, B. W. *Q. Rev. Chem. Soc.* **1968**, *22*, 527.

(20) Massart, R.; Contant, R.; Fruchart, J.; Ciabrini, J.; Fournier, M. *Inorg. Chem.* **1977**, *11*, 2916.