Under similar experimental conditions (1400 °C, 5 h), the pyrolysis of the poly(dimethylsilylene)diacetylene metal oxide composites in an argon atmosphere gave high yields of crystalline solid phases that contained the respective metal carbide and SiC. In all cases, the reaction with the metal oxide takes place at lower temperatures than with only carbon. 2) Variation of the poly(silylene)diacetylenes allows the modulation of the composition of the final ceramics as summarized for TiO2 (Table 3). When aryl groups are bonded to the silylene unit, ceramic residues containing higher amounts of TiC result (Table 3, run 3). In contrast, 1e, a polymer with two dimethylsilylene units, produces a ceramic with a TiC content of 57.1% (Table 3, run 2).

<table>
<thead>
<tr>
<th>Run</th>
<th>Polymer (equiv)</th>
<th>TiO2 (equiv)</th>
<th>Ceramic yield (%)</th>
<th>Composition (MC %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ia (4)</td>
<td>56</td>
<td>3 SiC-4 TiC (72.7)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ic (4)</td>
<td>60</td>
<td>6 SiC-4 TiC (57.1)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ie (4)</td>
<td>51</td>
<td>SiC-4 TiC (88.9)</td>
<td></td>
</tr>
</tbody>
</table>

Thus, we may expect to prepare a wide range of multi-phase ceramics of defined composition. Investigation of the potential of this method and the mechanistic implications are now under progress.

CAS Registry numbers:

(Received: March 17, 1992 [Z 5242 IE] German version: Angew. Chem. 1992, 104, 1228)

Organosaronato polyoxovanadium Clusters: Properties and Structures of the VIV Cluster [V204O24(O3AsC6H4-4-NH2)4]4− and the IV/V Cluster [H24V6O10(O3AsC6H6)8]2−

By M. Isaque Khan, Yuanda Chang, Qin Chen, Hakon Hope, Sean Parkin, D. P. Goshorn, and Jon Zubieta*

The chemistry of polyoxovanadium clusters incorporating group 5 elements has witnessed significant growth in recent years. Arsenic–vanadium clusters exhibit a variety of structural types of considerable topical interest1-10 and possess a range of stable cluster oxidation states as well as unusual magnetic properties.11-14 Furthermore, these heteropolyvanadates exhibit a pronounced tendency to form cage structures which may encapsulate neutral molecules or anions, a feature shared with a number of isopolynates such as [V11O22(H2O)]12−-17 [V14O36(SO4)]8−-15 [H2V8O44(X)]12− (X = Cl, Br, I),8-10 and [V15O36(CH3CN)]12−-11 and recently described for [V12As6O60(HCO3)]8− (η = 3.5,13 [V15As6O62(OH)8]12−-14 [V14As6O62(SO4)]8−-15 and [V14As6O62(0.3H2O)]8−-16 A related family of (organophosphonato)polyoxovanadium clusters constitutes a new class of layered compounds which can exhibit useful sorptive and catalytic properties,12-14 while the molecular polyoxides [H25V13O42(0.6PCH3)18-19] and [H25V16O42(0.1PCH3)18-19] provide examples of structures displaying cage and “wire” structural motifs, respectively. However, in contrast to this rapid development of the arsenic (and phosphonophanato)polyoxovanadium systems, the chemistry of oxovanadium clusters with organosaronates RAsO3− remains relatively unexplored, although one example of a layered structure [V20O42(C6H5AsO2H)2]·2H2O17 has been described. In this communication, we report two novel polyoxovanadium structural types found in the “oxidized” cluster I and the mixed valence cluster 2. The structures of these clusters illustrate the dramatic influences of small changes in ligand type upon the overall molecular geometry.

(TBA)2[NH4][V204O24(O3AsC6H4-4-NH2)4] 1
(TBA)2[H24V6O10(O3AsC6H6)8]2·2H2O 2
TBA = (n-C6H13)4N

Red, parallelepiped crystals of 1 were prepared in approximately 45% yield by heating a mixture of (NH4)2NaK2[V10O26], arsenic acid 4-NH4C6H5-AsO(OH)2, and (TBA)Br in methanol at reflux for 20 min. X-ray structure analysis of 18 revealed the presence of discrete (TBA)2N4 ions and NH4+ ions and a [V204O24(O3AsC6H4-4-NH2)4]4− whose structure is shown in Figure 1. The overall structure may be described as [V20O42(O3AsC6H4-NH2)2]3− toroid encapsulating a VO5− moiety. The toroid consists of three trinuclear [V15O35] units of edge-sharing octahedra with the conventional 60° angle formed by the V centers,19 which are linked through bridging oxo groups and the arsonato

5 SiC metal carbide ceramics have been recently obtained by the pyrolysis of poly(arsenosilane) metal powder composites: D. Seyfert, N. Bynson, D. P. Workman, C. A. Sobon, J. Am. Ceram. Soc. 1991, 74, 2687.
7 TiO2 particle size: < 100 nm.
9 The pyrolysis experiments were carried out on weighed samples (0.1 to 1 g) of the polymer metal oxide composite which were heated in an aluminum oxide boat (30 x 10 x 10 mm) with a gas-tight aluminum oxide tube (length 100 cm, diameter 30 mm) fitted with glass taps to allow the connection with a vacuum line. The argon flow was maintained at about 50 mL min−1. Experiments were performed in Eurotherm or Carboite furnaces (heating rate of 10 °C min−1 up to 1400 °C; then 5 h at 1400 °C). Ceramic yields (weight of polyoxlyride residue / 100) (weight of pyrolysis cage) × 100.
10 SiC and TiC were characterized by X-ray powder diffraction (Phillips diffractometer, CuKα radiation). The elemental analysis 48.20% Ti and 21.16% Si indicates the SiC-TiC phases to be present in a 3:4 ratio.
13 Simultaneous TGA and DTA analyses were performed in a stream of argon (50 mL min−1) with a Netzsch STA thermogravimetric analyzer interfaced with an Anasys 200 Debi-Nernag mass spectrometer (heating rate 10 °C min−1). TGA and DTA measurements were conducted with the Netzsch SW-STA-311, 001 software on a HP 9000-300 computer.
14 P. Pascal, Nouvelle Traité de Chémie Minérale, Masson, Paris; Gmelin
 ligands. The central vanadium atom V1 is in a highly distorted octahedral environment, in which the metal atom is displaced toward the O1-O2-O3 face; the average V-O (1,2,3) distance is 1.70(2) Å as compared to an average distance of 2.14(2) Å for V-O (4,5,6). This unusual oxometalate arrangement in I gives rise to four distinct types of oxy groups: terminal O atoms associated with the V centers of the nine-membered ring, μ2 oxy groups that bridge V atoms of the [V5O13] units, μ4 types that link the [V5O13] units to the central vanadium atom, and μ4 oxy groups which provide both the common vertex for the V octahedra of the trinuclear units and the link to the encapsulated V atom. Each organoarsinate group shares two of its oxygen atoms with vanadium centers of adjacent trinuclear units, while the third is bound to two vanadium centers in neighboring trinuclear units. The anion in I exhibits structural features common to polyanions exhibiting a central MO₆ octahedron[20-22] and to e-Keggin types.[23] The polyhedral representation of Figure 1b clearly shows the relationship of I to the Anderson [M₂O₄] clusters.[23] The structure of the anion in I may be best described as a double layer of polyhedra, one layer composed of the [V₅O₁₄]₃⁻ Anderson core and the second consisting of a [V₅(RAsO₃)₄]₃⁺ ring which rests on one face of the Anderson core.

Complex I undergoes a reversible one-electron reduction at -0.54 V to give the green-brown [V₅O₄(O₃AsC₆H₄-4-NH₂)₃]⁺⁻ which displays a broad EPR signal centered at g = 1.95. In contrast, chemical oxidation of I with hydrazines results in multiple-electron transfer coupled to proton transfer to give purple solutions of [V₆O₁₆(OH)₆(O₃AsC₆H₄-4-NH₂)₃]⁺⁻. Carefully controlled addition of the hydrazine reagents produces anions of intermediate reduction/protonation states. Such multiple electron/proton transfer processes appear to be characteristic of the chemistry of polyvanadates stabilized by organic ligands[30]

The reaction of (NH₄)₂NaN₃[V₆O₁₆] with C₆H₄AsO₂(OH)₂ in the presence of (TBA)Br quite unexpectedly resulted in partial reduction to give 2 as bright green crystals in 65% yield. The structure of 2[24] consists of discrete (TBA)⁺ ions and molecular anions of [H₂V₅O₁₆(O₃AsC₆H₄)₃]⁺⁻, shown in Figure 2a. Although the numerous examples of arsanatopolyoxovanadates studied to date in-

that of the anion in 1, the structure of the anion in 2 consists of a twisted 24-membered ring [V₆AsO₁₆] (Fig. 2b), which is highly distorted by the presence of additional intraring V-O-V and As-O-V bridges; the As-phenyl substituents, the ter-

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**References:**


[23] The polyhedral representation of Figure 1b clearly shows the relationship of I to the Anderson [M₂O₄] clusters.

[24] The reaction of (NH₄)₂NaN₃[V₆O₁₆] with C₆H₄AsO₂(OH)₂ in the presence of (TBA)Br quite unexpectedly resulted in partial reduction to give 2 as bright green crystals in 65% yield. The structure of 2[24] consists of discrete (TBA)⁺ ions and molecular anions of [H₂V₅O₁₆(O₃AsC₆H₄)₃]⁺⁻, shown in Figure 2a. Although the numerous examples of arsanatopolyoxovanadates studied to date in-

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**Figure 1:** a) Perspective views of the crystal structure of the anion in I. Left: View along the approximate threefold axis of the anion. Right: View perpendicular to this threefold axis. Selected bond lengths [Å]: V:ring-O(terminals), 1.56(4)–1.61(4); V:ring-O(µ³), 1.79(1)–1.86(1); V:ring-O(µ²), 1.95(2)–1.99(1); V:ring-O(µ¹), 2.28(1)–2.33(1); V-O(µ²), 2.10(1)–2.20(1); V-O(µ³), 1.60(1)–1.74(1); As-O(µ³), 1.65(2)–1.69(2); As-O(µ²), 1.72(2)–1.75(2); O1-V1-O6, 1.66(16); O2-V1-O4, 1.67(16); O3-V1-O5, 1.68(16). b) A polyhedral representation of the structure of the anion illustrating the stacking one ring of V octahedra and As tetrahedra.

**Figure 2:** a) Crystal structure of the anion in 2 (ORTEP). Selected bond lengths [Å]: V1-O1, 1.60(2); V1-O4, 1.97(2); V1-O5, 1.69(2); V1-O7, 2.04(2); V1-O9, 1.94(2); V2-O2, 1.57(3); V2-O4, 1.71(2); V2-O8, 1.98(2); V2-O10, 1.94(2); V2-O12, 1.93(2); V3-O3, 1.59(2); V3-O5, 1.99(2); V3-O11, 2.01(2); V3-O13, 1.99(2); V3-O14, 1.99(2); As1-O6, 1.79(3); all other As-O distances from 1.60(2) to 1.70(2) Å. b) A view of the [V₆AsO₁₆] ring of the anion. c) The
minal oxo groups of the vanadium atoms, and the hydroxyl groups of As1 and As1a project from this central ring. Alternatively, the structure may be described in terms of a layer structure of three \( \{V_2As_2O_7\} \) rings connected in a stacking fashion by \( \mu^2 \) oxo groups, as shown in Figure 2c.

The vanadium centers exhibit square-pyramidal geometry with the standard apical disposition of the terminal oxo groups. Each of the organoarsenate groups is bound to two oxygen atoms and contributes to the formation of the \( \{V_2As_2O_7\} \) rings, and four of them employ a third oxygen atom to coordinate to an adjacent ring. The remaining two organoarsenate groups participate in the outermost \( \{V_2As_2O_7\} \) rings, while the third oxygen atom of each is a terminal ligand. The latter oxygen atoms, O6 and O6a, are protonated. This assignment is based on the fact that the As3–O6 bond is long relative to the value anticipated for a terminal As=O bond, and the location of one peak in the difference electron density maps is consistent with a hydroxyl proton. The overall anionic charge of 2− requires the presence of four \( V^V \) and two \( V^V \) centers, an assumption confirmed by potentiometric titration. On the basis of valence sum calculations, the reduced sites are identified as V3 and V3a.

The presence of two reduced centers is confirmed by the magnetic properties of 2. This compound exhibits behavior characteristic of isolated \( V^2+ \) units. The temperature dependence of the magnetic susceptibility in the range 4.2 to 300 K follows the Blaney–Bowers equation[29] for isolated dimers containing two \( S = 1/2 \) cations with isotropic \( g \) tensors; the susceptibility displays a maximum at 20 K. The susceptibility data are consistent with extremely weak exchange coupling (2\( J_m = -9.1 \text{ cm}^{-1} \)) within vanadium dimers which are effectively isolated from each other. The magnetic data may be compared to that for \((VO^2+)\) systems in which \( J \) ranges from \(-25 \) to \(-250 \text{ cm}^{-1} \).[27] The weak exchange coupling in 2 is similar to that observed for \( VO(HPO_4) \cdot 0.5 H_2O \) and \( VO(HPO_4) \cdot 2H_2O \) salts which possess building blocks made up of two \( VO^2+ \) units with similar exchange networks. Furthermore, in contrast to 1, 2 undergoes two successive, facile, and reversible one-electron oxidations at +0.09 V and +0.46 V, which is consistent with the presence of two readily oxidized \( V^V \) centers. Thus, the cluster possesses magnetic and electron-transfer properties suggestive of a dimer \( \{V_2O_3(OAs_2C_2H_2)_3\} \) encapsulated and stabilized by sandwiching between two \( \{V_2O_3(OAs_2C_2H_2)_3\} \) fragments. While ligand-free polyoxometalates undergo almost exclusively cathodic processes, the introduction of organic ligands into the polyoxometalate framework allows the development of a more extensive electrochemistry by stabilizing a variety of "reduced" and mixed valence clusters with modified electron-storage add proton-transfer properties.[30]

The organoarsenate chemistry of vanadium appears to be remarkably diverse, such that relatively minor changes in substituents can produce dramatic structural differences as exemplified by 1 and 2. Furthermore, their electrochemical and magnetic properties suggest extensive electron storage and coupled electron–proton transfer in the chemistry of clusters of this type.

**Experimental Procedure**

1: Under an atmosphere of argon, (TBA)Br (2.58 g, 8 mmol) and arsenic acid (0.868 g, 4 mmol) were placed in a Schlenk tube fitted with a reflux condenser and were then dissolved in methanol (25 mL) (NH_4)_2As-K_2[V_2O_7] (0.56 g, 0.5 mmol) was added, and the resulting suspension was heated at reflux with stirring for 20 min whereupon a clear red-brown solution was obtained. After the hot solution was filtered and cooled to room temperature, it was stored at 4°C for 30 days. Crystalline crystals of 1 were collected by slow diffusion of CH_3CN into CH_2Cl_2.

CAS Registry numbers:
1. 142839-60-9, 142839-67-6, 4-CNCH_2CH_2As(OH)OH, 85-50-0; \( V_2O_3(OAs_2CH_2)_3 \), \( 100 \text{ cm}^{-1} \); \( V_2O_3(OH)As(OAs_2CH_2)_3 \), \( 100 \text{ cm}^{-1} \);
\( \text{CH}_3\text{CN}, 125\text{ cm}^{-1} \);
\( \text{CH}_3\text{CN}, 107\text{ cm}^{-1} \);
\( \text{CH}_3\text{CN}, 105\text{ cm}^{-1} \);
\( \text{CH}_3\text{CN}, 103\text{ cm}^{-1} \); \( V_2O_3(OAs_2CH_2)_3 \), \( 100 \text{ cm}^{-1} \).

Received: March 11, 1992 [Z 5235 IE]

German version: Angew. Chem. 1992, 104, 1236

[18] a) \( J_m = 1.085 \text{ cm}^{-1} \), \( V_2O_3(OAs_2CH_2)_3 \), \( 125 \text{ cm}^{-1} \); \( \mu(\text{Cu}) = 11.41 \text{ mm}^{-1} \), \( R = 0.087 \) for 5290 reflections with \( 2\theta < 108.5^\circ \) and \( z = 3 \) (Siemens S/3R diffractometer with rotating anode, Ni-filtered Cu radiation). The structure was solved using direct methods with the Siemens SHELXTL PLUS package. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2 (FRG), on quoting the depositary number CSD-56316, the names of the authors, and the journal citation.
Novel Polyether Copolymers Consisting of Linear and Dendritic Blocks

By Ivan Gitsov, Karen L. Wooley, and Jean M. J. Fréchet

Polyethylene glycols (PEGs), their derivatives and amphiphilic block copolymers have many applications as phase-transfer reagents, as compounds that could potentially encapsulate other materials and as emulsifying agents. Their properties arise from the existence of both hydrophilic and hydrophobic parts of the macromolecules. In spite of the promising results achieved up to now, the synthesis of novel polymers and copolymers of that type is still of importance due to the high demand for new materials with defined architecture and improved properties.

Recently, the synthesis of novel dendritic polyethers was reported. Because of their dense, but nonentangled structure these dendrimers are expected to impart unusual properties to other polymeric materials when incorporated in the polymer chain. This report explores the incorporation of these highly branched amorphous and hydrophobic dendrimers in a crystalline hydrophilic PEG as well as the properties of the resulting copolymers.

In a first approach PEG copolymers containing dendritic blocks were prepared by capping the ends of a, ω-bifunctional PEGs with dendrimers possessing a reactive functional group at their core. In order to estimate the influence of the size of the dendritic molecule on the reaction yields and the properties of the copolymers that are formed, dendrimers of the third ([G]-3-Br: 1) and fourth ([G]-4-Br: 2) generations were used (Scheme 1).

In order to avoid the association of acidic moieties with PEG and the incomplete conversion of some Williamson-type syntheses, the formation of the PEG dianion in situ by reaction with NaH was carried out in the presence of the dendritic bromide (Scheme 2) as described previously for the synthesis of PEG macromers.

![Scheme 1. The dendritic macromolecules employed in the reaction with the polyethylene glycol.](image1)

![Scheme 2. Synthesis of the copolymers.](image2)

In all cases investigated, the end-capping reaction proceeded smoothly at room temperature and was complete within 24 h. The length of the initial PEG block and the size of the dendritic bromide have no influence on the rate of formation of the copolymers. In contrast to the previously reported end-capping reactions of PEGs, the low molar ratio of the dendritic bromides to terminal hydroxyl groups (1.2:1) does not affect the yields, which remain over 90%.

The molecular weights of the starting materials and the resulting block copolymers are listed in Table 1. The molecular weights at the peak apex $M_n$ in the size-exclusion chromatography (SEC) traces are used as characteristic values for each product since they are less affected by low- and high-molecular weight impurities. The molecular weight distribution is calculated as the average of three measurements. It should be noted that most copolymers obtained have narrower molecular weight distributions than the initial PEGs, and all of them have apparent molecular weights lower than the values predicted for triblock copolymers of the type [Gm]-PEG-[Gm] (Table 1, Fig. 1). This difference between calculated and apparent molecular weights increases with the length of the initial PEG block.