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Vanadogermanate Cluster Anions

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Three novel vanadogermanate cluster anions have been synthesized by hydrothermal reactions. The cluster anions are derived from the $\{V_{18}O_{42}\}$ Keggin cluster shell by substitution of $V{=}O^{2+}$ "caps" by $Ge_2O(OH)_2^{4+}$ species. In $Cs_8[Ge_4V_{16}O_{42}(OH)_4]{\cdot}4.7H_2O$, **1**, (monoclinic, space group $C2/c$ (No. 15), $Z = 8$, $a = 44.513(2)$ Å, $b = 12.7632(7)$ Å, $c = 22.923(1)$ Å, $\beta = 101.376(1)°$) and $(pipH_2)_4(pipH)_4[Ge_8V_{14}O_{50}{\cdot}(H_2O)]$ (pip = $C_4N_2H_{10}$), **2** (tetragonal, space group $P4_2/nnm$ (No. 134), $Z = 2$, $a = 14.9950(7)$ Å, $c = 18.408(1)$ Å, two and four VO^{2+} caps are replaced, respectively, and each cluster anion encapsulates a water molecule. In $K_5H_8Ge_8V_{12}SO_{52}{\cdot}10H_2O$, **3**, (tetragonal, space group $I4/m$ (No. 87), $Z = 2$, $a = 15.573(1)$ Å, $c = 10.963(1)$ Å), four VO^{2+} caps are replaced by Ge_2O-$(OH)_2^{4+}$ species, and an additional two are omitted. The cluster ion in **3** contains a sulfate anion disordered over two positions. The cluster anions are analogous to the vanadoarsenate anions $[V_{18-n}As_{2n}O_{42}(X)]^{m-}$ (X = SO_3, SO_4, Cl; $n = 3$, 4) previously reported.

Introduction

A promising strategy for the synthesis of open framework and microporous structures is to connect polyoxometalate building units with other types of linking groups via covalent bonds. The linking groups can be organic molecules, simple metal cations, or complex cations. For example, several groups have used dicarboxylates to link isolated metal oxounits or metal oxide chains.[1-3] We have used metal cations to link preformed vanadium borophosphate anions into three-dimensional structures.[4] Others have synthesized compounds where polyoxovanadate anions are linked in a similar way.[5-7] The chain structures of $Na_{0.5}K_{6.5}[V_2O_2]$-$[Mo_8V_4O_{36}(VO_4)]{\cdot}12.5H_2O^{8}$ and $K_{12}[Ti_2O_2][SiNb_{12}O_{40}]{\cdot}16H_2O^{9}$ are examples of extended lattices where the cluster anions are linked by covalent bonds to oxygen atoms.

We are investigating the incorporation of silicate and germanate species into cluster anions that can be used to provide links to connect clusters into extended frameworks. In previous work, we reported the synthesis of the linear chain compound $Cs_{10.5}[(V_{16}O_{40})(Si_{4.5}V_{1.5}O_{10})]{\cdot}3.5H_2O^{10}$ in which two *trans* Si_2O_7 units in the cluster anion shell provide the connectors. Here, we report the synthesis of three vanadogermanate cluster anions that, although isolated, are the first examples that contain Ge_2O_7 anions incorporated into vanadate polyhedra based on the Keggin cluster anion.

The Keggin cluster anion with composition $\{M'O_4V_{12}O_{40}\}$ contains a shell of composition $\{V_{12}O_{36}\}$.[11] The enclosed tetrahedron completes the octahedral coordination of the 12 M cations. A second cluster anion type with the composition $\{V_{18}O_{42}\}$ can be derived from the Keggin shell by the addition of six VO^{2+} cations ("caps") to each of the square faces to form a convex polyhedron known as a rhombicuboctahedron. Rotation of the top part of this polyhedron by 45° results in a related polyhedron, the elongated square gyrobicupola, which has the same number of square and triangular faces. Examples of both polyhedra are known for vanadium polyoxoanions. Thus, $V_{18}O_{42}^{12-}$ first reported in

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Table 1. Summary of Compounds Derived from the Cluster Anion Shell $\{V_{18}O_{42}\}$

	ref.
V_{18} cluster shells	
$Na_{12}[V_{18}O_{42}(H_2O)]\cdot23H_2O$ — *a*	12
$Cs_9[H_4V_{18}O_{42}X]\cdot12H_2O$ (X = Br, Cl) — *a*	13
$K_9[H_4V_{18}O_{42}X]\cdot16H_2O$ (X = Cl, Br, I) — *a*	13
$Na_6[H_9V_{18}O_{42}VO_4]\cdot21H_2O$ — *b*	14
$(NH_4)_8[V_{18}O_{42}SO_4]\cdot25H_2O$ — *b*	14
As_2O derivatives	
$K_6[As_6V_{15}O_{42}(H_2O)]\cdot8H_2O$ — *b* $-3VO + 3As_2O$	14
$(NH_4)_6[As_8V_{14}O_{42}(X)]$ (X = SO_3^{2-}, SO_4^{2-}) — *b* $-4VO + 4As_2O$	14
$[N(CH_3)_4][As_8V_{14}O_{42}(H_2O)]$ — *b* $-4VO + 4As_2O$	14, 15
$Rb_5[As_8V_{14}O_{42}Cl]\cdot2H_2O$ — *b* $-4VO + 4As_2O$	16
$Na_5[As_8V_{12}O_{40}(HCO_2)]\cdot18H_2O$ — *b* $-6VO + 4As_2O$	17
$M_2O(OH)_2$ derivatives, M = Si, Ge	
$Cs_{10.5}[V_{16}O_{40}](Si_{4.5}V_{1.5}O_{10})\cdot3.5H_2O^c$ — *b* $-2VO + 2Si_2O_3$	10
$Cs_8[Ge_4V_{16}O_{42}(OH)_4]\cdot4.7H_2O$ — *a* $-2VO + 2Ge_2O_3$	*d*
$(C_4N_2H_{11})_8[H_4Ge_8V_{14}O_{50}(H_2O)]$ — *b* $-4VO + 4Ge_2O_3$	*d*
$K_5[H_8Ge_8V_{12}SO_{52}]\cdot10H_2O$ — *b* $-6VO + 4Ge_2O_3$	*d*

a Elongated square gyrobicupola. *b* Rhombicuboctahedron. *c* Chain structure. *d* This work.

the compound $Na_{12}V_{18}O_{42}\cdot24H_2O$ is an example of the latter as are the anions $[H_4V_{18}O_{42}X]^{9-}$, X = Cl, Br, I (see Table 1). In contrast, in $NH_4[V_{18}O_{42}(SO_4)]\cdot25H_2O$ and Na_6H_9-$[V_{18}O_{42}(VO_4)]\cdot21H_2O$ the cluster anions have the rhombicuboctahedral topology.

The $V_{18}O_{42}$ cluster ion shell also forms the basis for several other compounds in which the VO^{2+} cation formally is replaced by a different cationic species with the same "footprint". The rhombicuboctahedral vanadoarsenate anions $[V_{18-n}As_{2n}O_{42}(X)]^{m-}$ (X = SO_3, SO_4, Cl; n = 3, 4) are the earliest example of this type of substitution in which three or four VO_5 square pyramids are replaced by $As(III)_2O_5$ groups. A related example is the anion $[V_{12}As_8O_{40}(HCO_2)]^{3-}$ which has two missing VO^{2+} caps. From the perspective of building extended structures, the substitution of $As(III)_2O_5$ units is not useful because the weakly coordinating As(III) lone pairs effectively terminate the structure, and consequently, our focus has been on developing the substitution chemistry of $M(IV)_2O_7$ units (M = Ge, Si) which can act as linking groups.

Materials and Methods

All reagents were used as purchased from Aldrich (GeO_2, $VOSO_4$, CsOH, KOH, and piperazine) and EM Science (ethylene glycol). Infrared spectra were recorded on a Mattson FTIR 5000 spectrometer within the range $400-4000$ cm^{-1} using the KBr pellet method. Thermogravimetric analyses (TGAs) were carried out in air at a heating rate of 2 °C/min, using a high resolution TGA 2950 thermogravimetric analyzer (TA Instruments). Elemental analyses were performed at Galbraith Laboratories, Knoxville, TN, or by electron microprobe analysis using a JEOL 8600 electron microprobe operating at 15 keV with a 10 μm beam diameter and a beam current of 30 nA.

Synthesis. $Cs_8[Ge_4V_{16}O_{42}(OH)_4]\cdot4.7H_2O$, 1. Compound **1** was synthesized from a mixture of the following solutions: 0.2 M GeO_2, 0.5 M $VOSO_4$, and 5.7 M CsOH. The GeO_2 solution was prepared by dissolving 1.046 g of GeO_2 in a mixture of ethylene glycol and deionized H_2O (4:1 volume ratio). The solution was then stirred for 24 h. The $VOSO_4$ solution was prepared by dissolving 5.821 g of vanadyl sulfate hydrate in deionized water. The CsOH solution

was used as purchased. The reactant solutions were added into a Teflon liner in the ratio of 3 mmol GeO_2/0.6 mmol $VOSO_4$/1.2 mmol CsOH. The initial pH was measured to be 8.7. The liner was placed into a Parr autoclave, which was then sealed. The reactants were heated at 170 °C for 3 days and then quenched to ambient conditions. The final pH was ~9−10. A single-phase product in the form of brown needle crystals was recovered by filtration and washed with deionized water (yield 30% based on vanadium). IR (cm^{-1}): 3400 (s), 1633 (m), 977 (s), 823 (s), 754 (s), 678 (s), 601 (m). Electron microprobe analysis gave the ratio V/Ge = 4.02 as expected for the composition $Cs_8[Ge_4V_{16}O_{42}\cdot(OH)_4]\cdot4.7H_2O$ determined from the X-ray diffraction data. The vanadium-to-germanium ratio was also determined by chemical analysis and found to be 3.97 in agreement with the other data. Thermogravimetric analysis indicated a continuous weight loss beginning immediately and continuing up to 350 °C. The weight loss observed between 100 and 350 °C (3.98%) was in good agreement with the weight loss calculated for loss of 4.7 water molecules per formula unit and complete dehydroxylation (4.03%). Above 350 °C, the weight increased due to partial oxidation of V(IV) to V(V) oxide.

$(pipH_2)_4(pipH)_4[Ge_8V_{14}O_{50}\cdot(H_2O)]$, 2. Compound **2** was synthesized by reaction of a mixture of GeO_2 (0.1569 g, 1.5 mmol), $VOSO_4$, (0.2333 g, 1 mmol), piperazine (0.8708 g, 10 mmol), and 2 mL of deionized H_2O, (111 mmol). The reactants were heated in a stainless steel Parr autoclave at 170 °C for 4 days. The reaction was quenched to room temperature and the product filtered and washed with deionized water. A single phase consisting of olive brown polyhedral crystals was obtained (yield 45% based on vanadium). The initial and final pH values of the reaction mixture were ~9−10. IR (cm^{-1}): 3438 (w), 3313 (w), 3282 (w), 3253 (w), 3167 (w), 3032 (w), 2844 (w), 2756 (w), 2642 (w), 1624 (w), 1514 (w), 1460 (w), 1373 (w), 1329 (w), 1211 (w), 1167 (w), 1117 (w), 1084 (w), 989 (s), 781 (s), 756 (s), 681 (wm), 634 (wm), 567 (m), 484 (w), 434 (w). Anal. Found: 26.1% V, 19.4% Ge, 13.8% C, 3.6% H, 8.0% N. Calcd for $(pipH_2)_4(pipH)_4[Ge_8V_{14}O_{50}\cdot(H_2O)]$: 25.3% V, 20.6% Ge, 13.7% C, 3.4% H, 8.0% N. Themogravimetric analysis in air showed decomposition to occur in three broad steps between 150 and 520 °C. The overall weight loss of 25.8% is in good agreement with the value of 25.1% calculated with the formula and assuming the residue to be $Ge_8V_{14}O_{51}$ with complete oxidation of vanadium(IV) to vanadium(V).

$K_5H_8Ge_8V_{12}SO_{52}\cdot10H_2O$, 3. Compound **3** was synthesized by hydrothermal reaction in a Teflon bag. The reactants, 11.68 M KOH (0.43 mL, 5 mmol), GeO_2 (0.5027 g, 4.8 mmol), and 1 M $VOSO_4$ (2 mL, 2 mmol), were added to the Teflon bag. The bag was then sealed and placed in a 1-L Parr autoclave. The reaction was heated at 180 °C for 4 days. Upon quenching of the reaction to ambient temperature, the product was filtered and washed with deionzied water. Compound **3** was obtained as a minor phase in the form of brown rectangular crystals mixed with major phases of blue and white powders. IR (cm^{-1}): 3421 (s), 1793 (w), 1646 (w), 1626 (w), 1385 (w), 1327 (w), 1117 (m), 989 (m), 908 (w), 785 (s), 700 (vw), 636 (s), 600 (m), 526 (m), 498 (m).

Crystal Structure Determinations for 1, 2, and 3. The crystal structures of **1**, **2**, and **3** were determined from single crystal X-ray diffraction data. Crystals were mounted on glass fibers and measured on a Siemens SMART platform diffractometer fitted with 1K CCD area detector and graphite monochromatized Mo Kα radiation at 293 K. A hemisphere of data (1271 frames at 5 cm detector distance) was collected for each phase using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 30−40 s/frame. The first 50 frames were remeasured at the end

Table 2. Crystallographic Details for **1**, **2**, and **3**

	1	2	3
empirical formula	$H_{13.4}Cs_8Ge_4O_{50.7}V_{16}$	$C_{32}H_{96}N_{16}V_{14}Ge_8O_{51}$	$K_5H_{28}Ge_8V_{12}SO_{62}$
fw	2993.4	2815.2	2439.8
space group, Z	$C2/c$ (No. 15), 8	$P4_2/nnm$ (No. 134), 2	$I4/m$ (No. 87), 2
a, Å	44.513(2)	14.9950(7)	15.573(1)
b, Å	12.7632(7)	14.9950(7)	15.573(1)
c, Å	22.923(1)	18.408(1)	10.963(1)
β, deg	101.376(1)	90	90
V, Å^3	12768(1)	4139.0(4)	2658.8(4)
T, K	293(2)	293(2)	293(2)
λ, Å	0.71073	0.71073	0.71073
ρ_{calcd}, g/cm^3	3.111	2.260	3.047
μ(Mo Kα), mm^{-1}	8.66	4.46	7.02
R1[a]	0.079	0.049	0.038
wR2[b-d]	0.184	0.134	0.088

[a] $R = \Sigma||F_o| - |F_c|/\Sigma|F_o|$ (based on reflections with $I > 2\sigma(I)$). [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0992P)^2 + 364.1P]$; $P = [(F_o^2) + 2F_c^2]/3$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0870P)^2 + 4.915P]$; $P = [\max(F_o^2,0) + 2F_c^2]/3$. [d] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0576P)^2]$; $P = [\max(F_o^2,0) + 2F_c^2]/3$.

of data collection to monitor instrument and crystal stability. The data were integrated using the Siemens SAINT program.[18] The program SADABS was used for the absorption correction.[19] The structures were solved by direct methods and refined by using the SHELXTL program.[20] Crystallographic data are given in Table 2 and selected bond lengths and bond valence sums given in Tables 3 and 4.

For **1**, both the germanium vanadate clusters and the intercluster species were found to be disordered. In the cluster, one position occupied by the $[Ge_2O_7]$ dimer is ordered while two other positions are disordered and occupied either by a $[Ge_2O_7]$ dimer or a $[VO_5]$ square pyramid. The ratio $[Ge_2O_7]/[VO_5]$ was refined to ~ 0.64 and 0.38 for the two disordered positions, respectively. Most of the cesium and water oxygen positions were found to have fractional occupancies. The thermal parameters of the water oxygen positions were fixed at the same value in order to refine their relative occupancies. The refined unit cell content gives the formula $Cs_8[Ge_4V_{16}O_{42}(OH)_4]\cdot 4.7H_2O$. No attempt was made to locate the hydrogen atoms.

The refinements of the structures of **2** and **3** were straightforward. For **2**, the hydrogen atoms of the protonated piperazine cations were located by geometric methods and refined with geometrical constraints. The hydrogen atoms were not located for the hydroxyl groups or for the water molecules that are disordered between two positions inside the cluster anion.

For **3**, the SO_4 tetrahedron at the cluster center was found to be randomly disordered between two orientations. The K(2) atom position is split, and all water positions have fractional occupancies.

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Table 3. Selected Bond Distances (Å) for **1**, **2**, **3**

1

Ge1−O36	1.742(8)	Ge3−O31	1.70(1)	Ge5−O47	1.71(2)
Ge1−O4	1.743(8)	Ge3−O40	1.72(2)	Ge5−O42	1.753(11)
Ge1−O33	1.746(8)	Ge3−O23	1.736(9)	Ge5−O6	1.779(9)
Ge1−O34	1.770(8)	Ge3−O39	1.824(10)	Ge5−O21	1.799(10)
Ge2−O14	1.729(8)	Ge4−O41	1.730(15)	Ge6−O31	1.699(10)
Ge2−O38	1.731(8)	Ge4−O43	1.733(10)	Ge6−O48	1.71(4)
Ge2−O2	1.737(8)	Ge4−O22	1.761(9)	Ge6−O22	1.750(10)
Ge2−O34	1.775(8)	Ge4−O39	1.804(10)	Ge6−O42	1.892(12)
V1−O39	1.435(11)	V6−O33	2.039(9)	V12−O5	1.944(8)
V1−O18	2.018(11)	V7−O24	1.612(9)	V12−O15	1.949(8)
V1−O23	2.050(11)	V7−O10	1.925(8)	V12−O6	1.966(8)
V1−O43	2.093(12)	V7−O9	1.932(9)	V13−O30	1.610(10)
V1−O31	2.095(12)	V7−O25	1.943(8)	V13−O9	1.916(9)
V2−O42	1.545(10)	V7−O2	2.040(9)	V13−O1	1.939(8)
V2−O6	1.936(9)	V8−O32	1.617(9)	V13−O25	1.970(9)
V2−O21	2.003(10)	V8−O8	1.930(9)	V13−O18	1.980(9)
V2−O22	2.018(10)	V8−O13	1.936(8)	V14−O11	1.623(9)
V2−O31	2.072(10)	V8−O22	1.980(9)	V14−O7	1.896(8)
V3−O17	1.614(8)	V8−O23	1.997(9)	V14−O28	1.914(8)
V3−O1	1.923(8)	V9−O27	1.628(10)	V14−O33	1.995(8)
V3−O7	1.931(8)	V9−O26	1.931(9)	V14−O14	1.999(8)
V3−O25	1.948(8)	V9−O16	1.935(8)	V15−O46	1.623(9)
V3−O14	2.018(8)	V9−O5	1.942(8)	V15−O26	1.939(9)
V4−O29	1.606(10)	V9−O21	1.956(9)	V15−O10	1.942(9)
V4−O26	1.928(9)	V10−O12	1.623(9)	V15−O9	1.966(9)
V4−O21	1.958(10)	V10−O5	1.906(8)	V15−O43	1.988(10)
V4−O31	1.987(10)	V10−O15	1.925(8)	V16−O19	1.622(9)
V4−O43	1.996(10)	V10−O16	1.927(8)	V16−O8	1.920(8)
V5−O20	1.611(8)	V10−O4	2.014(8)	V16−O3	1.959(8)
V5−O10	1.904(8)	V11−O44	1.595(9)	V16−O22	1.971(9)
V5−O16	1.917(8)	V11−O7	1.934(8)	V16−O6	1.979(9)
V5−O4	1.996(9)	V11−O8	1.948(8)	V17−O37	1.617(9)
V5−O2	2.033(8)	V11−O13	1.951(9)	V17−O13	1.927(9)
V6−O45	1.630(8)	V11−O28	1.977(8)	V17−O1	1.934(8)
V6−O3	1.907(8)	V12−O35	1.615(9)	V17−O23	1.984(9)
V6−O28	1.928(8)	V12−O3	1.935(8)	V17−O18	1.987(9)
V6−O15	1.939(8)				

2

Ge−O5	1.728(4)	Ge−O4	1.761(4)	Ge−O7	1.763(3)
Ge−O2	1.751(4)				
V1−O9	1.595(8)	V2−O4	1.994(4)	V4−O6	1.607(6)
V1−O4	1.991(4)	V3−O3	1.604(6)	V4−O1	1.928(4)
V2−O8	1.593(6)	V3−O1	1.925(4)	V4−O2	2.004(4)
V2−O1	1.937(4)	V3−O2	2.003(4)		

3

Ge−O2	1.770(2)	Ge−O6	1.734(3)	Ge−O7	1.726(3)
Ge−O5	1.736(3)				
V1−O3	1.587(5)	V2−O1	1.835(3)	V2−O7	2.041(3)
V1−O7	1.971(3)	V2−O4	1.594(3)	V2−O8	2.420(7)
V1−O5	1.985(3)	V2−O5	2.037(3)	S−O8	1.451(7)
V2−O1	1.826(3)				

Table 4. Bond Valence Sums for **1**, **2**, and **3**

1

V1[a]	4.67	V7	4.09	V13	4.15
V2[a]	4.11	V8	4.06	V14	4.18
V3	4.11	V9	4.14	V15	4.04
V4	4.06	V10	4.14	V16	4.06
V5	4.09	V11	4.21	V17	4.08
V6	4.07	V12	4.14		

2

V1	3.95	V3	4.12	V4	4.07
V2	4.09				

3

V1	4.07	V2	4.61

[a] The V1 and V2 sites are partially occupied with site occupancies of 0.32 and 0.64, respectively.

The thermal parameters of the water oxygen positions were fixed at the same value in order to refine their relative occupancies. The hydrogen atoms were not located.
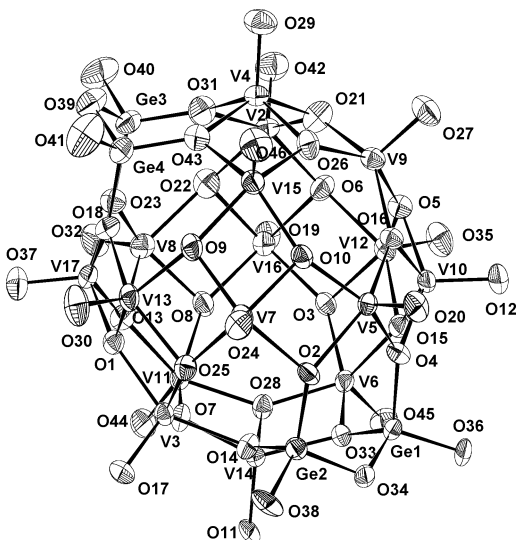
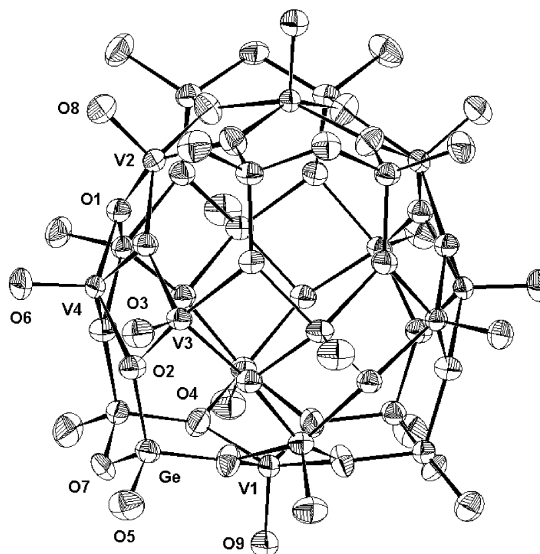**Figure 1.** Cluster ion in **1** showing the atom labeling. Thermal ellipsoids are shown at 50% probability.
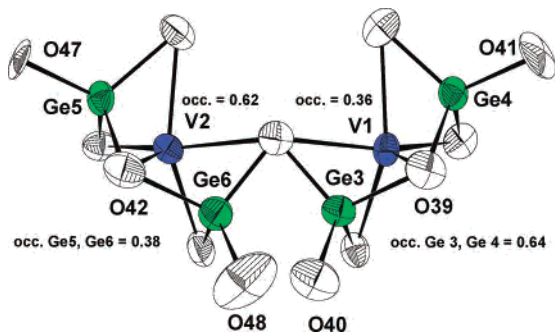
Figure 2. Disordered VO_5 and Ge_2O_7 units in the **1** anion.

Discussion

The structure of **1** is derived from the $\{V_{18}O_{42}\}$ cluster ion shell with the elongated square gyrobicupola topology. Two of the VO caps are replaced by $Ge_2O(OH)_2$ dimers as shown in Figures 1 and 5. One of the $Ge_2O(OH)_2$ units is ordered while the second is disordered over two positions with refined occupancies of 0.38 and 0.64. The $V1O_5$ and $V2O_5$ square pyramidal units are disordered over the same two positions as shown in Figure 2. Ge1 and Ge2 have bond valence sums (BVSs) of 3.98 and 4.06 v.u. and bond lengths in the range 1.729(8)–1.775(8) Å. The longest Ge–O bond lengths, 1.770(8) and 1.775(8) Å, are to the oxygen atom (O34) corner-shared between the two tetrahedra. The bond valence sums for the two disordered $Ge_2O(OH)_2$ units are 4.06, 3.92, 3.89, and 3.92 as expected with Ge–O bond lengths in the range 1.72(2)–1.824(10) Å for Ge3 and Ge4 and 1.699(10)–1.892(12) Å for Ge5 and Ge6. As in the ordered $Ge_2O(OH)_2$ unit, the longest Ge–O bonds are to the shared oxygen atoms between the two tetrahedra, O39 and O42. The $Ge6O_4$ tetrahedron, which is one of the pair with the lower site occupancy, is the most distorted.

With the exception of V1 which has the lowest site occupancy, all of the VO_5 square pyramids have apical V=O lengths of 1.545(10)–1.630(8) Å and V–O bond lengths of 1.916(9)–2.040(9) Å in the pyramid bases. The bond valence sums for all of the vanadium atoms, with the

exception of V1 that is poorly defined because of its low occupancy, indicate that the average oxidation state of vanadium is close to 4.0. Refinement of the occupancies of the cesium positions, in addition to the disordered positions in the cluster anion, gives a composition of $Cs_8Ge_4V_{16}O_{42}$-$(OH)_4 \cdot 4.7H_2O$ in agreement with an average oxidation state corresponding to V(IV). A water molecule (Ow7, occupancy 0.51) is located in the center of the cluster anion.

The clusters are arranged in layers in the *bc* plane of the unit cell. Within each layer, the cluster anions are arranged such that the ordered $Ge_2O_5(OH)_2$ units are oriented on the same side of the layer; adjacent clusters in the same layer are related by the *c* glide operation. Anions in adjacent layers have opposite orientations, and there are four layers per unit cell. The cesium cations and water molecule occupy sites between cluster anions.

The compound **2** contains the second example of a cluster anion derived from the $\{V_{18}O_{42}\}$ cluster ion shell with four of the VO "caps" replaced by four Ge_2O_3 units in an ordered way to give a cluster anion of composition $\{Ge_8V_{14}O_{50}\}$ as shown in Figures 3 and 5. In this case, and unlike **1**, the geometry corresponds to the rhombicuboctahedron. The Ge_2O_3 dimers occupy positions that are related by a $\bar{4}$ axis.

The Ge–O bond lengths range from 1.728(4) to 1.763(3) Å, and the Ge–O bond valence sum is 3.97 v.u. as expected. The VO_5 square pyramids have typical geometries with apical and basal VO bond distances in the ranges 1.593(6)–1.607(6) Å and 1.925(4)–2.004(4) Å, respectively. The BVSs indicate that all vanadium atoms have V(IV) oxidation states. Two water molecule sites were located, both inside of the cluster anion and partially occupied. One water molecule (site O10B) is weakly bonded to V (2.29(6) Å), and the other water molecule is disordered about a position at the center of the cluster anion. The total occupancy corresponds to one water molecule per cluster.

The piperazinium cations were located with reasonable bond lengths but are somewhat disordered as indicated by the thermal parameters. The large thermal ellipsoids obtained

Figure 3. Cluster ion in **2** showing the atom labeling. Thermal ellipsoids are shown at 50% probability.
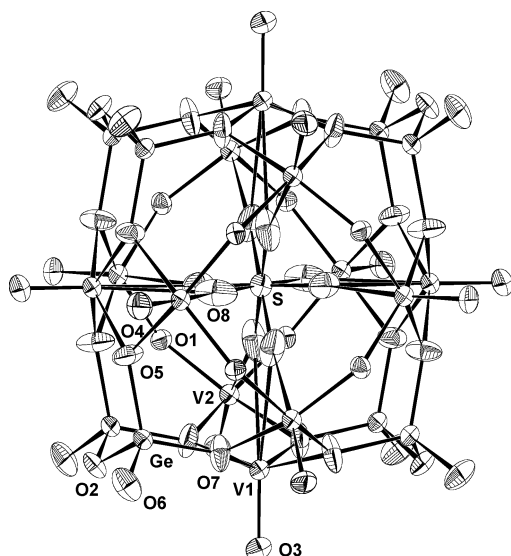
Figure 4. Cluster ion in **3** showing the atom labeling. Thermal ellipsoids are shown at 50% probability.

from the refinement are indicative of static disorder, but a model with split atom positions was not used in order to limit the number of variables. The two nitrogen atoms in the piperazinium cations are inequivalent. One nitrogen atom (N1) is in hydrogen bonding distance of the terminal oxygen atom bonded to Ge (O5−N1 = 2.750(10) Å) and is presumably protonated, accounting for eight protons per cluster anion. The four additional protons that are required for charge neutrality, assuming the composition determined by both chemical analysis and the structure refinement and that all the vanadium atoms are in the V(IV) oxidation state, are presumed to protonate half of the other nitrogen atoms (N2) in a disordered way. The N2 atoms are not within distances of any of the oxygen atoms appropriate for hydrogen bonds.

The cluster anions are arranged in the unit cell to form a body centered arrangement in a $2a \times 2b \times 2c$ supercell. The piperazinium cations occupy the interstitial space between the cluster anions. The composition of **2** is (pipH$_2$)$_4$-(pipH)$_4$[Ge$_8$V$_{14}$O$_{50}$·(H$_2$O)].

The structure of **3** is also based on the {V$_{18}$O$_{42}$} shell with rhombicuboctahedral symmetry, Figures 4 and 5. Four of the VO caps are replaced by four Ge$_2$O(OH)$_2$ dimers, and two are omitted completely to give a cluster shell of composition {H$_8$V$_{12}$Ge$_8$O$_{48}$}. The center of the shell contains

a SO$_4^{2-}$ anion that is disordered equally over two orientations. The four oxygen atoms of the sulfate anion form long bonds (2.420(8) Å) with four V2 atoms and complete a distorted octahedron. The V1 atoms are square pyramidally coordinated. The BVS for the single Ge atom is 4.08 v.u., and the Ge−O distance to the bridging oxygen atom (O2) has the longest bond length (1.770(2) Å). The square pyramidally coordinated vanadium atom (V1) has a BVS of 4.07 v.u. and typical V(IV)−O apical (1.587(5) Å) and basal distances (1.971(3) Å and 1.985(3) Å). In contrast, the BVS for V2, 4.61 v.u., indicates that this site is occupied by both V(IV) and V(V) cations. This is apparent in the larger range of distances. The vanadium oxygen atom coordination can be viewed as arising from a local (111) displacement of the vanadium atom toward one triangular face of an octahedron of oxygen atoms.

Two potassium sites were located in the structure refinement. K1 is eight coordinated by oxygen atoms at a distance of 2.828(3) Å that are shared with V2 atoms. The other potassium cation site is split between two positions. Potassium ions in both sites are nine coordinate by seven oxygen atoms and two water molecules. The overall composition K$_5$H$_8$Ge$_8$V$_{12}$SO$_{52}$·10H$_2$O indicates an average oxidation state of vanadium of 4.42 in excellent agreement with the value predicted from the bond valence sums $(4.07 + 2 \times 4.61)/3 = 4.43$.

The cluster anions are stacked along the c axis and are connected into columns by the potassium−oxygen bonds. The channels formed between the columns are occupied by the water molecules. Ten water molecules per formula unit in four partially occupied sites were located. All of the water molecules are within hydrogen bonding distances of the Ge$_2$O(OH)$_2$ dimers and the O6 oxygen atom of the V2=O unit.

A summary of the known compounds derived from the cluster anion shell {V$_{18}$O$_{42}$} is presented in Table 1. Examples are now known in which 2, 3, and 4 VO caps are replaced by As$_2$O$_3$, Si$_2$O$_5$, or Ge$_2$O$_5$ dimers. The substituted derivatives all have the rhombicuboctahedral topology with **1** being the one exception. Prediction of which topology will be adopted for a particular composition is not yet possible, though the rhombicuboctahedron appears to be favored by the presence of a central tetrahedrally coordinated cation. The energetic differences between the two possible arrangements are small, and additional examples are needed to
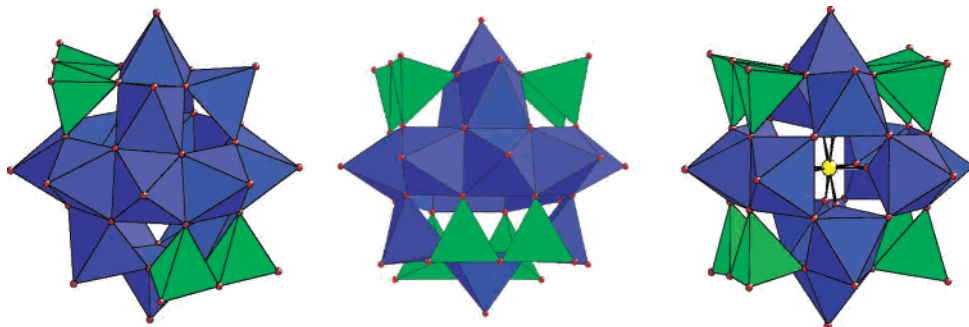
Figure 5. Polyhedral representations of the cluster ions in (a) **1**, (b) **2**, (c) **3**. Only one of the two disordered Ge$_2$O$_7$ units is shown in (a). VO$_5$ polyhedra are blue, GeO$_4$ polyhedra are green, and S is yellow.

develop a better understanding of the factors that control the cluster geometry.

Supporting Information Available: Three X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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