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New Crown-Shaped Polyoxovanadium(V) Cluster Cation with a μ_6-Sulfato Anion and Zwitterionic μ-(β-Alanine): Crystal Structure of $[V_6O_{12}(OH)_3(O_2CCH_2CH_2NH_3)_3(SO_4)][Na][SO_4]\cdot 13H_2O$

Chew Hee Ng,*,† Chai Wei Lim,† Siang Guan Teoh,‡ Hoong-Kun Fun,§ Anwar Usman,§ and Seik Weng Ng‖

School of Arts and Science, Tunku Abdul Rahman College, 53300 Kuala Lumpur, Malaysia,
School of Chemical Sciences, and X-ray Crystallography Unit, School of Physics,
Universiti Sains Malaysia, 11800 Penang, Malaysia, and Institute of Postgraduate Studies,
University of Malaya, 50603 Kuala Lumpur, Malaysia

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Treatment of vanadium(V) oxide with an ethanol-concentrated sulfuric acid mixture, followed by the addition of an equimolar amount of β-alanine and sodium hydroxide, and finally raising the pH to 3.9 with sodium carbonate solution, under continuous heating in a water bath and in the presence of air, leads to the polyionic sodium cyclo-{μ_6-(sulfato-*O*,*O*′,*O*′′)tris[μ-(β-alanine-*O*,*O*′)-μ-oxo]-tris(μ-hydroxo-μ-oxo)hexa[oxovanadium(V)]} sulfate tridecahydrate which crystallizes in the monoclinic $P2_1/n$ space group [$a = 9.5192(4)$, $b = 20.1185(9)$, $c = 22.6174(9)$ Å, $\beta = 97.011(1)°$; $Z = 4$]. The crown-shaped polyoxovanadium(V) cluster cation, with carboxylate-bridging amino acid ligands, has an Anderson structure with two unique capping sulfato ligands. Its structural analysis, together with IR, UV–vis, and preliminary data on its solution properties, is presented.

Mononuclear oxovanadium complexes[1,2] and polyoxovanadates[3,4] have attracted extensive interest owing to their biological and medical activity and their application as new materials in catalysis and sensor technology. Oxovanadium clusters are generally anionic polyoxovanadate compounds.[5] A change in the negative charge of the oxovanadium cluster can be effected by protonation or substitution of the oxo linkages, as well as by encapsulation of charged entities.[5,6] The structural chemistry of the polyoxovanadium cluster has been enriched by both the variability in the coordination polyhedra adopted by vanadium (tetrahedron, square pyramid, trigonal bipyramid, octahedron) and the substitution of the peripheral oxo groups of the parent polyvanadate core by oxygen-bearing anions, such as phosphate, alkoxide, and carboxylate.[4−7] Among the oxovanadium clusters with carboxylate ligands, the title complex is the first example that involves a carboxylic acid residue that possesses an amino group.

V_2O_5 (2 g, 0.01 mol) was heated with stirring in a mixture of ethanol and concentrated sulfuric acid (15 cm^3) in a water bath for 1 h. β-Alanine (1.96 g, 0.02 mol) and NaOH (0.88 g, 0.02 mol) were dissolved in a small volume of water, and the solution was then added to the vanadium solution. Heating was continued for another 3 h. The reaction was conducted in air. The pH was raised from ∼0.5 to pH 3.9 by the dropwise addition of Na_2CO_3 solution, and the mixture was heated for an additional 2 h. The dark blue solution (λ_{max}, 768 nm), when left to cool overnight, deposited purple crystals (1.9 g, 15% yield). A 0.42 × 0.22 × 0.08 mm^3 specimen was used in the room-temperature diffraction measurements on a Siemens CCD area-detector diffractometer (Mo Kα radiation). The structure was solved by SHELXS-97 and refined by SHELXL-97. Non-hydrogen atoms were refined anisotropically. The carbon- and nitrogen-bound hydrogen atoms were generated geometrically; the water hydrogen atoms were not included in the refinements. The refinements converged to $R = 0.059$ and $wR = 0.152$ for the 7324 of the 10 843 reflections beyond the $I > 2\sigma(I)$ threshold. An absorption correction was performed using SADABS program.[8] The crystal data are listed in Tables 1 and 2.

Anal. Calcd (Found) for $C_9H_{50}N_3O_{42}S_2V_6$: C, 8.54 (8.99); H, 3.98 (4.23); N, 3.32% (3.39%). FTIR (KBr, cm^{-1}): ν(O−H) 3404(s), 3226(s); $\nu_{as}(COO^-)$ 1579(s), $\nu_s(COO^-)$ 1453(s); 1505(m), 1340(w); ν(S−O) 1200(sh), 1118(s),

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* Author to whom correspondence should be addressed. E-mail address: ngch@mail.tarc.edu.my.

† Tunku Abdul Rahman College.

‡ School of Chemical Sciences, Universiti Sains Malaysia.

§ X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia.

‖ University of Malaya.

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Table 1. Crystal Data for $[V_6O_{12}(OH)_3(O_2CCH_2CH_2NH_3)_3(SO_4)][Na][SO_4]\cdot 13H_2O$

empirical formula	$C_9H_{50}N_3NaO_{42}S_2V_6$	V	4299.1(3) Å^3
fw	1265.27	Z	4
space group	$P2_1/n$	wavelength	0.710 73 Å
unit cell	$a = 9.5192(4)$ Å	density (calcd)	1.955 g m^{-3}
	$b = 20.1185(9)$ Å	abs coeff	1.483 mm^{-1}
	$c = 22.6174$ Å	R	0.0593
	$\beta = 97.011(1)°$	R$_w$	0.1518

Table 2. Selected Bond Length Ranges (Å) and Angles (deg) for $[V_6O_{12}(OH)_3(O_2CCH_2CH_2NH_3)_3(SO_4)][Na][SO_4]\cdot 13H_2O$

VO$_6$ polyhedra[a]		SO_4^{2-} (H-bonded)	
V−O$_V$	1.597−1.607(3)	S2−O−O(unbonded)	1.467−1.475(4)
V−O$_E$(oxo)	1.969−2.037(3)	S2−O(H-bonded)	1.498(3)
V−O$_E$(hydroxo)	1.978−2.007(3)	Na1−O14	2.484(4)
V−O$_E$(β-alanine)	2.012−2.040(3)	Na1−O11^{i} [b]	2.417(4)
V−O$_T$(sulfato)	2.315−2.489(3)	V−O(S1)−V	89.5−94.0(1)
μ_6-SO_4^{2-}		V−O(oxo)−V	100.1−118.4(2)
S1−O1	1.451(3)	V−O(hydroxo)−V	100.1−101.9(1)
S1−O(bridging)	1.474−1.486(3)	O24−V1−O2	77.2(1)
		O20−V1−O23	92.6(1)

[a] Vanadyl bond, V−O$_V$; equatorial bond, V−O$_E$; trans bond, V−O$_T$. [b] Symmetry operation i: $x - {}^1/_2$, ${}^1/_2 - y$, $z - {}^1/_2$.

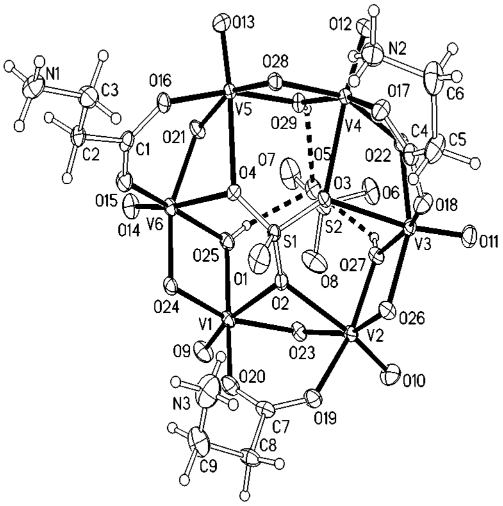

Figure 1. Plot of cluster cation $[V_6O_{12}(OH)_3(O_2CCH_2CH_2NH_3)_3(SO_4)]^+$ with SO_4^{2-} counterion as 50% probability ellipsoids.

1053(s); ν(V═O) 963(s); ν(V−O) 701(m), 635(s), 590(s), 533(s); δ(V−O) 427(m). UV−vis (1 M sulfuric acid) λ, nm (δ, M^{-1} cm^{-1}): 765 (13). The solid sample is not stable on prolonged exposure to air or moderate heating; it is not soluble in water but dissolves in mineral acids. Solution of sample in 1 M H_2SO_4 oxidizes iodide to iodine.

The crystal structure of the title compound consists of a vanadium(V) cluster cation, a sodium cation, a sulfato anion, and lattice water molecules. The six independent vanadium atoms are hexacoordinate in distorted octahedral geometries (Figure 1). The cluster cation, from a count of the number of vanadyl, equatorial, and trans bonds, can be designated as being [1+4+1]-coordinated.[9] Although these bonds are in the range observed for V^VO_6 polyhedra with one vanadyl bond,[9] the vanadyl bond falls near the upper limit of V^V═O distances reported for mononuclear oxovanadium complexes.[10] The equatorial bonds, V^V−O(μ-oxo) and V^V−O(μ-hydroxo), are somewhat longer than those reviewed by Khan and Zubieta.[5]

Figure 2. Schematic representation of the six VO$_6$ octahedra. Black circles denote the oxygen atoms that are hydrogen bonded to the μ_6-sulfato group.

The cluster cation can also be regarded as being built by laterally fusing together six octahedra so as to enclose a central cavity (Figure 2). Protruding out from one face of the approximate plane are the three μ-(β-alanine-*O*,*O′*) entities and one μ_6-(sulfato-*O*,*O′*,*O″*) group, which give rigidity to the structure. The unprecedented μ_6-sulfato group appears to serve as the templating unit for cluster assembly and to stabilize the oxovanadium core. Another sulfato ion lies on the other side of the assembly, and its oxo-atom (O5) is H-bonded to three hydroxo ligands. The cavity is capped by this ion. The bonding modes of the two sulfato ions have extended the types of bonding modes exhibited by the sulfato ion in other systems.[11,12]

The apical oxo atoms, O14 and O11 in **1**, are linked to Na1 and Na1^{ii}, respectively, (symmetry operation ii: ${}^1/_2 + x$, ${}^1/_2 - y$, ${}^1/_2 + z$) to generate a polyionic chain. The sodium ion is also hexacoordinate, and it is bonded to four water molecules.

The V_6O_{24} core has an Anderson structure (isopolymetalate containing a crown of six octahedrons sharing edges). It is, thus, similar to those found in the oxovanadium(IV) cluster anion[13] $[(V^{IV}O)_6(CO_3)_4(OH)_9]^{5-}$ and other anionic Anderson species[4] such as $[Mo_8O_{26}]^{4-}$ and $[CoW_6As_6O_{30}]^{4-}$. In the latter two species, the capping ligands are MoO_4^{2-} and cyclo-$As_3O_3^{3-}$, respectively. However, the present polyoxovanadium core differs from the more common V_6O_{19} core found in oxovanadium(V) cluster anions[5,14] such as $[V^V{}_6O_{13}\{(OCH_2)_3CMe\}_2]^{2-}$ and $[V^V{}_6O_{11}(OH)_2\{(OCH_2)_3CR\}_2]$.

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Supporting Information Available: One X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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