A Spherical Potassium-Capped Vanadium Methylphosphonate as Another ε-Keggin Fragment, $[H_6KV_{12}O_{27}(VO_4)(PO_3CH_3)_3]^{5-}$

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An $[H_3KV_{12}O_{27}(AsO_4)_4]^{6-}$-isostructural ε-Keggin fragment anion, $[H_6KV_{12}O_{27}(VO_4)(PO_3CH_3)_3]^{5-}$, was photochemically prepared. This K^+-capped anion is formally built of nine $V^{IV}O_6$ octahedra, three PO_3C tetrahedra, and four V^VO_4 tetrahedra, one of the latter being a central VO_4^{3-} group. The capping K^+ cation lies on the C_3 axis and links two adjacent anion, to form a linear chain of the anions along c-axis.

An ε-Keggin fragment complex capped by a K^+ cation, $K_6[H_3KV^{IV}_4V^V_8O_{27}(AsO_4)_4]{\cdot}8H_2O$, has been prepared by reduction of an aqueous solution of vanadate(V) with thiocyanate in the presence of As^{5+}.[1] The $[H_3KV^{IV}_4V^V_8O_{27}(AsO_4)_4]^{6-}$ anion is formally built up by nine VO_6 octahedra and four AsO_4 tetrahedra to form the spherical chiral ε-Keggin fragment (with replacement of C_3-occupying three VO_6 octahedra by AsO_4 tetrahedra) which is stabilized by capping K^+ and by three VO_4 tetrahedra, as shown in Figure 1 where four vanadium(IV) centers in the anion have been characterized to be localized on three filled circles as localized V^{IV} sites and fourth V^{IV} as delocalized over three hatched circles.[2] The valence bond summations suggest that the terminal O atoms in each of the three C_3-occupying AsO_4 groups are protonated.

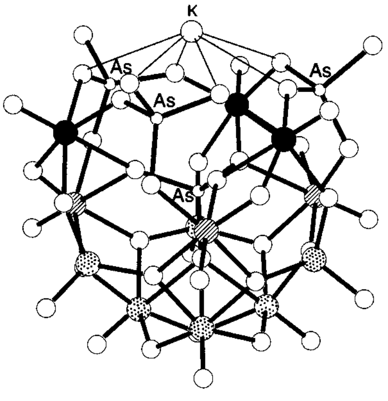

Figure 1. Structure of $[H_3KV_{12}As_3O_{39}(AsO_4)]^{6-}$.

We found that an isostructural vanadium methylphosphonate (with different V^{IV}/V^Vmixed-valency) is formed as $K_5[H_6KV^{IV}_9V^V_3O_{27}(V^VO_4)(PO_3CH_3)_3]{\cdot}16.5H_2O$ (**1**), when a source of methylphosphonate ($[PO_3CH_3]^{2-}$) anion replaces arsenate in the reduction processes. It is notable that the family of the above ε-Keggin fragments is commonly stabilized by a capping potassium cation and by additional three VO_4 tetrahedra. The present paper describes the photochemical synthesis and crystal structure of **1** as another high-nuclearity species of the K^+-capped ε-Keggin fragment.

1 was prepared according to the modification of our previous method:[3] solids of $[Bu^tNH_3]_4[V_4O_{12}]$[4] (0.45 g), $CH_3PO_3H_2$ (0.27 g), and $C_6H_5PO_3H_2$ (0.50 g) were stirred in a water (18 mL)/CH_3OH (2 mL) solution, and the yellow solution (pH ≈ 1.9) was adjusted to pH = 5.1 by KOH. The resulting dark-yellow solution was moved into a Pyrex tube (volume: 20 mL) and UV-irradiated by a 500 W super-high-pressure mercury lamp without filter for 6 days. Brown prismatic solids of **1** were obtained (yield: 56 % based on V). Found: H, 2.42; C, 2.09; P, 5.1; K, 12.2; V, 34 %. Calcd for $H_{48}C_3O_{56.5}P_3K_6V_{13}$: H, 2.45; C, 1.82; P, 4.70; K, 11.86; V, 33.48 %. Potentiometric redox titrations with $KMnO_4$ showed that the V^{IV}:V^V ratio is ≈ 9:4. IR spectrum of **1** (Figure 2) (ν [cm^{-1}] = 2925, ν(C–H); 1310, ν(P–C); 1094 and 1050, ν(P–O); 1011, ν(P–O or V=O); 967, ν(V=O); 819 and 701, ν(V–O–V)) displays a characteristic pattern of metal methylphosphonates.[5,6] Since the absence of $C_6H_5PO_3H_2$ brought about no formation of **1**, $C_6H_5PO_3H_2$ seemed to be essential for the photochemical preparation of **1**, probably as both additional reductant and buffer. The photochemical formation of the discrete anion $[H_6KV_{12}O_{27}(VO_4)(PO_3CH_3)_3]^{5-}$ in the $C_6H_5PO_3H_2/CH_3PO_3H_2$-mixed system is in contrast to the hydrothermal synthesis in the $V_2O_3/C_6H_5PO_3H_2/CH_3PO_3H_2$ system which gave a layered vanadium phosphonate, $VO(C_6H_5PO_3)_{1-y}(CH_3PO_3)_y{\cdot}1.5H_2O$ (y= 0.5, 0.75).[7]

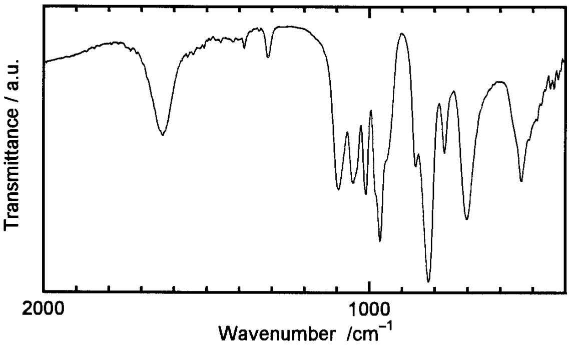

Figure 2. IR spectrum of **1**.

Figure 3 shows the structure of anion of **1**,[8] which can be derived formally from $[H_3KV_{12}As_3O_{39}(AsO_4)]^{6-}$ (Figure 1) by replacing three peripheral four-coordinate As–OH groups by $P–CH_3$ groups and a central tetrahedrally coordinated As atom by V atom. The bond valence sum (BVS) calculations[9] suggest that nine and four V atoms for VO_6 octahedra (BVS = 3.9–4.0) and VO_4 tetrahedra (4.9–5.0) are V^{IV} and V^V, respectively, being in agreement with the result (V^{IV}:V^V = 9:4) of the manganometric titration.[10] Furthermore, BVS values for O7 (1.1) and O9 (1.1) atoms suggest that six μ_2-O atoms of O7, O7^i, O7^{ii}, O9, O9^i, and O9^{ii} are protonated.

Temperature dependence of the product of χT for **1** is shown in Figure 4 where χ is the molecular magnetic susceptibility and T the temperature.[11] χT decreases gradually on decreasing temperature, and makes a plateau in the range

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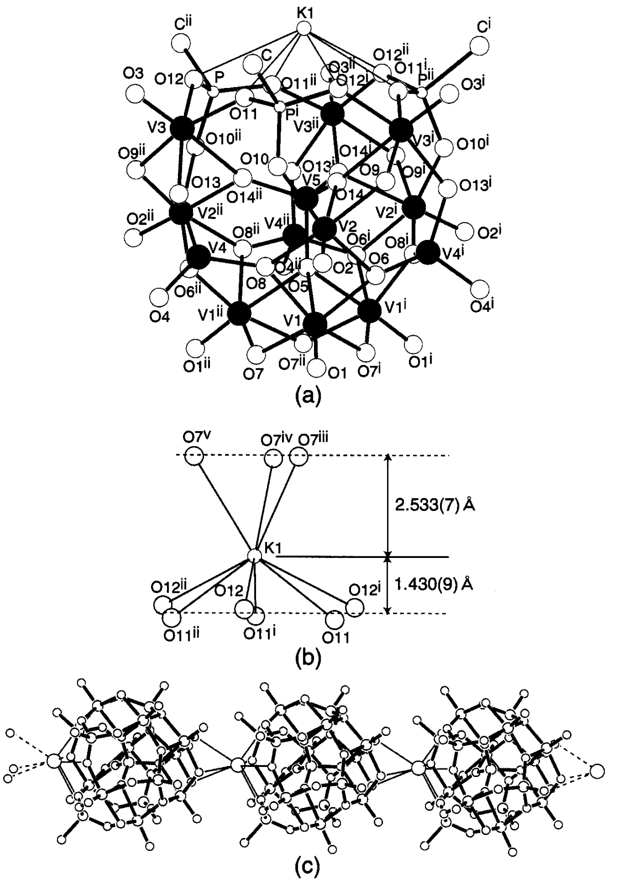

Figure 3. Views of [H$_6$KV$_{12}$O$_{27}$(VO$_4$)(PO$_3$CH$_3$)$_3$]$^{5-}$ anion (a), coordination environment of K1 (b), and linear chain structure of the anions in **1** (c). Least-squares planes defined by [O11, O11^{i}, O11^{ii}, O12, O12^{i}, O12^{ii}] and [O7^{iii}, O7^{iv}, O7^{v}] are denoted by dashed lines in (b). Symmetry codes: (i) -x+y+1, -x+1, z; (ii) -y+1, x-y, z; (iii) x, y, z-1; (iv) -x+y+1, -x+1, z-1, (v) -y+1, x-y, z-1.

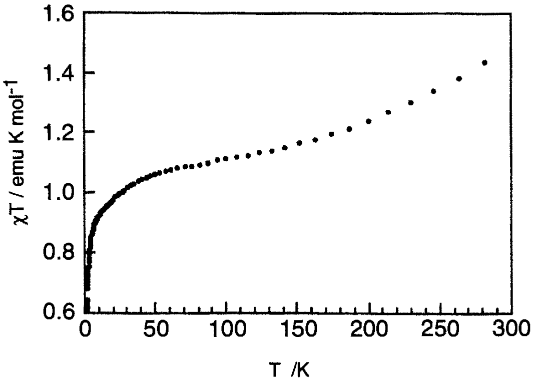

Figure 4. Temperature dependence of χT for **1**.

70–150 K. Below 50 K χT decreases rapidly. The value of χT in the range 70–150 K, 1.1 emu mol^{-1} K, is close to the value (1.13 emu mol^{-1} K) expected for three localized V^{IV} centers, implying V^{IV} centers on the C_3-occupying V3, V3^{i}, and V3^{ii} atoms in V···V distances of 5.610(7) Å as a result of three sets of the antiferromagnetic coupling between V1 and V2 centers in short V···V distance of 2.966(4) Å, compared with the shortest V···V distance 3.281(4) Å between symmetry-related V2 and V3 atoms. The value of χT at room temperature (1.5 emu mol^{-1} K) suggests the presence of five uncoupled V^{IV} centers, probably on three V3 atoms as localized V^{IV} sites and other two V atoms as delocalized over three V1 sites in V···V distance of 3.330(7) Å and V2 sites in 5.986(9) Å for each.

The capping K1 atom is on the C_3-axis and coordinated by nine oxygen atoms. The six-coordinative oxygens O11 and O12 (in K···O distances of 2.87(1) and 3.16(1) Å respectively) and symmetry-related ones define the plane, and the K1 atom lies 1.430(9) Å above this plane. The seven-to-nineth coordination positions are occupied by terminal O7 atom (in K···O distance of 3.00(1) Å) and its symmetry-related ones which belong to a neighboring anion, to form a linear chain of the anions along the *c*-axis (Figure 3(c)). This is in strong contrast to the case of K$_6$[H$_3$KV$^{IV}_4$V$^{V}_8$O$_{27}$(AsO$_4$)$_4$]·8H$_2$O which showed a zigzag chain arrangement of linked anions due to different four oxygens O1, O2, O6, and O4^{i} atoms in a neighboring anion.[1] The above K1 atom is coordinated by all the nine O atoms belonging to the anions. On the other hand, K2 atom is coordinated by two crystal water molecules and five anion-O atoms with K···O distances of 2.67(1)–3.25(1) Å, and bridge the two symmetry-related anions. Similarly, K3 atom is coordinated by three crystal water molecules and four O atoms belonging to the same anion with K···O distances of 2.69(5)–3.11(1) Å.

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8 A single crystal of **1** with 0.32 × 0.12 × 0.09 mm coated with an epoxy resin was sealed in a glass capillary and mounted on Rigaku AFC-5S four-circle diffractometer with monochromatized Mo Kα (λ= 0.71069 Å) radiation. Crystal data: H$_{48}$C$_3$O$_{56.5}$P$_3$K$_6$V$_{13}$, MW= 1978.13, trigonal, $P\bar{3}$ (No. 147), a = 19.06(3), c = 10.676(5) Å, Z = 2, D_c = 1.955 gcm^{-3}, F(000)= 1952, μ(Mo Kα)= 2.263 mm^{-1}. Of the 16980 total reflections, 12381 were unique. Structure was solved by SHELXS86 and refined based on 2777 observed reflections with I > 3σ(I) and 157 variables. Absorption correction DIFABS was applied with transmission factors from 0.417 to 0.816. The final discrepancy factors were R_1= 0.092 and wR_2= 0.097. C, P, K, and V atoms were refined anisotropically. Since the refinement of K3 and O16 with full occupancy resulted in large thermal parameters (≈13 and 44 Å^2, respectively), their site occupancies were fixed at 2/3 and 1/2, respectively.
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10 The ^{51}V NMR spectrum of **1** was measured in D$_2$O solution (0.07M) on a 300-MHz spectrometer (JEOL AL300) at 298 K (standard: NaVO$_3$), and showed two broad bands at –644.0 ppm ($\nu_{1/2}$= 995 Hz) and –660.3 ppm ($\nu_{1/2}$= 885 Hz) with an 1.00:0.27 intensity ratio, probably due to V^{V} sites in the three capping and one central VO$_4$ tetrahedra. The integrated intensities of the two resonance bands were estimated by a curve fitting technique due to their overlapping.
11 The magnetic susceptibility in the range 4–300 K was measured under the magnetic field of 1.0 T with a Quantum Design, MPMS-5S SQUID Magnetometer. The experimental data were corrected for diamagnetic contributions using standard Pascal constants.