

Synthesis and characterization of a polyoxovanadate cluster representing a new topology

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A new type of mixed-valence polyoxoanionic cluster, $[V_{13}^V V_{3}^{IV} O_{42}(Cl)]^{8-}$, composed of 14 $\{VO_5\}$ square pyramids and 2 $\{VO_4\}$ tetrahedral units, hosting a chloride ion has been synthesized and characterized.

Polyoxometalates constitute a fascinating class of inorganic systems that is unmatched in structural diversity, reactivity, and relevance to such areas as analytical chemistry, materials science and catalysis, nanotechnology, chemical sensing, environmental decontamination, biochemical and geochemical processes, and medicine.¹ Polyoxovanadates, or vanadium oxide clusters, are a prominent subclass of polyoxometalates which, as compared to polyoxomolybdates and polyoxotungstates, are relatively under-investigated.² In recent years, a number of polyoxovanadate clusters exhibiting diverse topologies and interesting structural and electronic properties have been reported. They include $[V_4O_{12}]^{4-}$, $[V_5O_{14}]^{3-}$, $[V_{10}O_{28}]^{6-}$, $[V_{12}O_{32}]^{4-}$, $[V_{13}O_{34}]^{3-}$, $[V_{15}O_{36}]^{5-}$, $[V_{15}O_{42}]^{9-}$, $[V_{16}O_{38}]^{7-}$, $[V_{17}O_{42}]^{4-}$, $[V_{18}O_{42}]^{12-}$, $[V_{19}O_{49}]^{9-}$ and $[V_{34}O_{82}]^{10-}$.^{3–14} These clusters may contain fully oxidized, reduced, or mixed-valence vanadium centers and can act as host systems for a variety of neutral or anionic guest species. The encapsulated guest species may exert templating effects influencing the electronic and framework structures of the host metal-oxide shells.

In the course of our ongoing investigation¹⁵ of the potential of polyoxovanadate clusters as structural motifs for the preparation of metal-oxide based extended structure materials, we have prepared a mixed-valence vanadium oxide cluster, $[V_{13}^V V_{3}^{IV} O_{42}(Cl)]^{8-}$, containing a hitherto unknown vanadium oxide framework structure. This report describes the synthesis and characterization by FTIR spectroscopy, elemental analysis, thermogravimetric analysis, manganometric titration, bond valence sum calculation, temperature dependent magnetic properties studies, electron paramagnetic resonance, and complete single crystal X-ray diffraction analysis of the new compound, $[V_{13}^V V_{3}^{IV} O_{42}(Cl)] \cdot 8C_5H_5NH \cdot 4H_2O$ (**1**).

In a typical synthesis, a mixture of $C_{11}H_{26}N_2O_6$ (1,3-bis{tris[hydroxymethyl]methylamino}propane), H_2O , C_5H_5N , $COCl_2$ and NH_4VO_3 in the molar ratio 1:149.3:6.07:1.99:1.09 is heated at 90 °C for 19 hours to give dark green crystals of **1** in good yield.[†]

The structure[‡] of the anionic $[V_{16}O_{42}(Cl)]^{8-}$ cage in **1**, projected approximately down the *b*-axis of the monoclinic unit cell, is

shown in Fig. 1. The cage has crystallographic twofold symmetry, but approaches closely to *mm2* (C_{2v}) symmetry. It may be described as formed by the fusion of 14 $\{VO_5\}$ square pyramids and two $\{VO_4\}$ tetrahedra. As is common in polyoxovanadate cages, each of the five-coordinate vanadium atoms has a single terminal oxygen atom, with its remaining four oxygens participating in the cage framework. The tetracoordinate vanadiums are bound to two terminal and two framework oxygen atoms, which is a less common situation.

The V–O framework bonds define four distinct types of environments within the cage for the seven independent five-coordinate vanadium atoms. One of these atoms (V1) is bound to four μ_3 -O atoms with V–O distances ranging from 1.823(3) to 1.903(3) Å. Two vanadiums (V2 and V4) are linked to one μ_2 -O [V–O = 1.704(3) and 1.706(3) Å] and three μ_3 -O atoms [V–O = 1.909(3) to 2.026(3) Å]. Three vanadium atoms (V3, V5, and V6) form bonds to two μ_3 -O [V–O = 1.956(3) to 2.018(3) Å] and two μ_2 -O atoms [1.779(3) to 1.818(3) Å]. Finally, V7 is bound to four μ_2 -O atoms, with V–O distances between 1.822(3) and 1.973(3) Å. The terminal oxo–V distances for these seven metal atoms all lie within the narrow range of 1.597(3) to 1.608(3) Å.

The tetrahedral vanadium atom V8 is bound to two μ_3 framework oxygen atoms [V–O = 1.819(3) and 1.832(3) Å] and

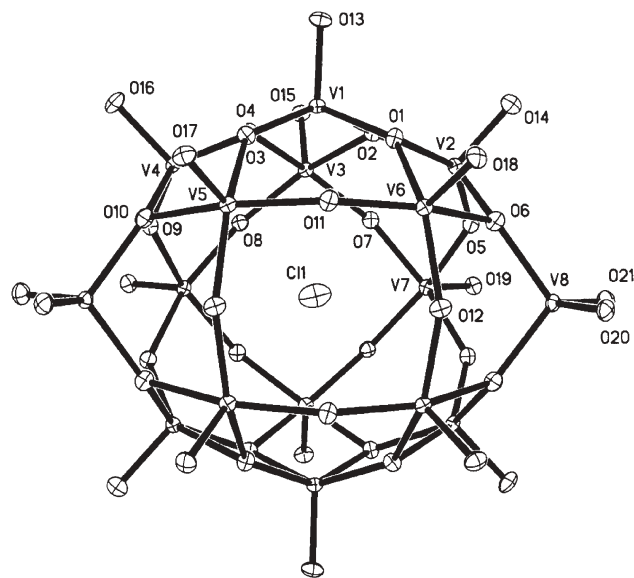


Fig. 1 A view of the anion cluster $[V_{13}^V V_{3}^{IV} O_{42}(Cl)]^{8-}$ in the crystals of **1** showing the atom labelling scheme. Thermal ellipsoids are drawn at the 50% probability level. The cluster has imposed twofold crystallographic symmetry. The Cl^- at the center of the cluster also lies on the twofold axis.

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two terminal oxygen atoms [V–O = 1.633(3) and 1.647(3) Å]. All bond angles at V8 are within 2° of their ideal tetrahedral values.

The negatively charged vanadium oxide shell in **1** hosts a chloride ion at its center. There is no covalent interaction of this ion with the atoms in the vanadium oxide framework, as shown by its average distance of 3.630 Å from the vanadium atoms of shell. The encapsulation of chloride and bromide ions has been previously observed in the negatively charged vanadium oxide shells [V₁₅O₃₆]⁵⁻ and [H₄V₁₈O₄₂]⁸⁻.

A {V₁₆O₄₀} core, composed of pyramidal {VO₅} units and encapsulating a water molecule has been observed in the extended structure chain compound Cs_{10.5}{V₁₆O₄₀}{Si_{4.5}V_{1.5}O₁₀}·3.5H₂O.¹⁶ Also, a {V₁₆O₃₈} shell has been observed in a three-dimensional open-framework solid, [{Cu(1,2-pn)₂}₇{V₁₆O₃₈(H₂O)}₂]₂·4H₂O,¹⁷ made of {V₁₆O₃₈(H₂O)}⁷⁻ clusters interlinked by {Cu(1,2-pn)₂}²⁺ groups, and more recently in the discrete cluster {V₁₆O₃₈(Cl)}⁸⁻.¹⁰ Unlike the shell observed in **1**, the {V₁₆O₃₈} shell in these compounds contains 16 {VO₅} square pyramids that share edges and corners. The topology of the vanadium oxide shell in **1** is totally different and unprecedented.

Fig. 2 shows a view of the unit cell contents of the crystals of **1**. Charge is balanced by the presence of eight pyridinium ions, two of which are disordered, per cage. There are also four water molecules of crystallization per {V₁₆O₄₂} unit, which participate in hydrogen bonds to both cluster oxygen atoms (e.g., O7···O22 [at (x, 1 - y, z - ½)] 2.799 Å, O18···O22 [at (-x, ½ - y, 1 - z)] 2.879 Å) and pyridinium N–H groups ions [e.g.,

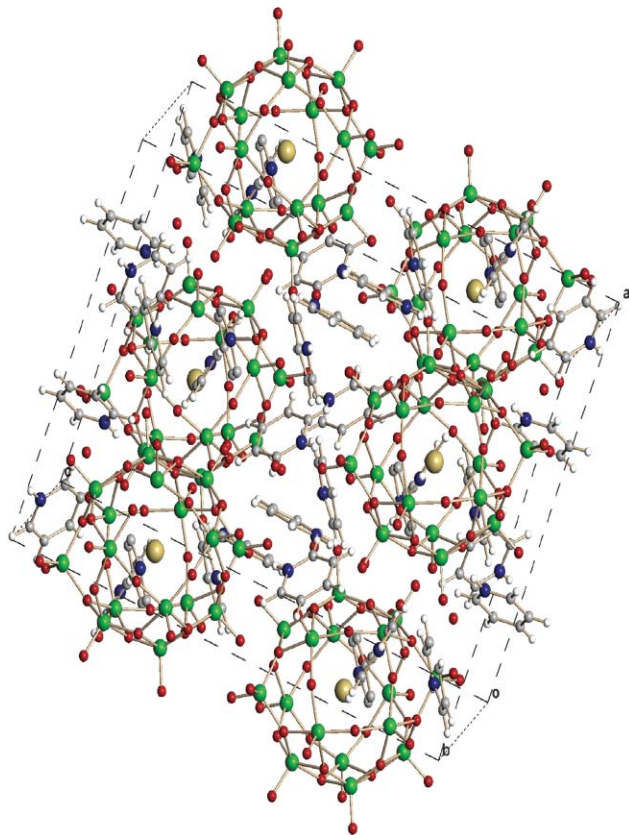


Fig. 2 A view of the unit cell contents in the crystals of [V^V₁₃V^{IV}₃O₄₂(Cl)]·8C₅H₅NH₂·4H₂O (**1**).

O22···H33(N3) = 1.86 Å]. This network of hydrogen bonds may play a role in the insolubility of **1** in water and common organic solvents.

The results of the bond valence sum calculation and manganometric titration of reduced vanadium (V^{IV} sites) indicate the presence of three V^{IV} sites per formula unit which is consistent with the formulation and charge balance requirements of **1**. The temperature dependent magnetic measurement results are presented in Fig. 3.¹⁸ The compound exhibits Curie paramagnetism. The data were fitted to the Curie–Weiss law at high temperature:

$$\chi = \chi_0 + \chi_{\text{TI}} = [C/(T - \theta)] + \chi_{\text{TI}} \quad (1)$$

The best fit was $C = 0.96$ emu K/(Oe mol), $\theta = 3.25$ K, $\chi_{\text{TI}} = 0.00083$ emu/(Oe mol). The effective magnetic moment ($\mu_{\text{eff}} = \sqrt{8\chi_0 T}$) at 300 K is 2.79 μ_{B} corresponding to three V^{IV} ions. The EPR spectrum of the compound has one resonance line with $g = 1.97$.

Thermogravimetric analysis¹⁹ of **1** reveals a three-step weight loss accounting for 38.5% mass of the compound. The first weight loss between 45–130 °C corresponds to the loss of four solvate water molecules. The second weight loss, between 130–330 °C, corresponds to the loss of the eight pyridinium ions. The last step between 330–430 °C corresponds to the removal of the chloride ion. There was no further weight change up to 800 °C. The IR spectrum of the black residue exhibits medium intensity bands at 678, 532, and 450 cm⁻¹ indicating a reduced vanadium oxide phase that has not been further characterized.

In summary, we have discovered a mixed-valence polyoxovanadate cluster representing a new vanadium oxide framework structure. Presence of potentially reactive {VO₄} units on the cluster surface make it an attractive building block for nanostructured materials¹⁵ derived from these motifs.

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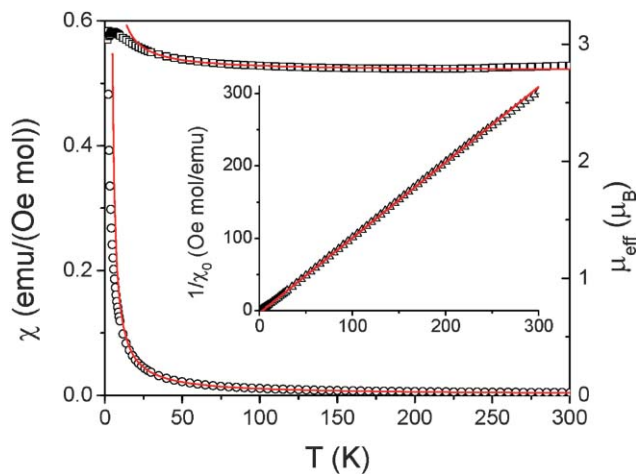


Fig. 3 Dependencies of the magnetic susceptibility (○), effective magnetic moment (□) and reverse susceptibility (Δ) of **1** on temperature T . The lines drawn through the data are the fits to the Curie–Weiss law.

Notes and references

† A mixture of 1,3-bis[tris(hydroxymethyl)methylamino]propane (2.3 mmol), H₂O (333.34 mmol, 6 mL), pyridine (1.13 mL, 13.97 mmol), phosgene (4.57 mmol, 2.42 mL of 20% w/w solution in toluene), and NH₄VO₃ (2.5 mmol) were placed in a 23 ml Parr Teflon-lined autoclave. The mixture was stirred for 30 seconds (pH = 5.1) and heated inside an electric furnace maintained at 90 °C for 19 hours. The oven was turned off and the autoclave cooled slowly for 24 hours to 25 °C inside the oven. The dark green crystals of **1** were filtered from the light brown color mother liquor (pH = 4.8). The crystals of **1** were dried in air at room temperature to give 240 mg pure material (~69% based on vanadium). Anal. Calc. for **1**: C, 21.49; H, 2.53; N, 5.01; Cl, 1.59; V, 36.46. Found: C, 20.82; H, 1.95; N, 4.51; Cl, 1.96; V, 35.35%. Prominent IR bands (KBr pellet, 4000–400 cm⁻¹): 3415 s, 2923 m, 1631 m, 1483 m, 975 vs, 767 m, 745 m, 678 m cm⁻¹.

‡ Crystal data for **1**: C₄₀H₅₆ClN₈O₄₆V₁₆, *M* = 2235.42, monoclinic, space group *C2/c*, *a* = 16.205(4), *b* = 20.186(5), *c* = 22.101(5) Å, β = 91.94(3)°, *V* = 7225(3) Å³, *Z* = 4, *T* = 173(2) K, *D*_c = 2.055 Mg m⁻³, μ = 2.105 mm⁻¹, *F*(000) = 4420, crystal size = 0.17 × 0.16 × 0.11 mm³. A total of 37616 reflections (1.84 ≤ θ ≤ 28.29°) were collected, of which 8698 unique reflections were used for structural elucidation (*R*_{int} = 0.0427). The final *R*₁ was 0.0596 (all data). CCDC depository number 269613. See <http://dx.doi.org/10.1039/b507531a> for crystallographic data in CIF or other electronic format.

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- 18 The magnetic data were recorded on a 39.2 mg polycrystalline sample of **1** in the 2–300 K temperature range using a Quantum Design MPMS-5S SQUID spectrometer. Calibrating and operating procedures have been reported elsewhere [C. J. O'Connor, *Prog. Inorg. Chem.*, 1979, **29**, 203]. The temperature dependent magnetic data were obtained at a magnetic field of *H* = 1000 Oe, and the diamagnetic background from the sample holder was corrected.
- 19 The thermogravimetric analysis was performed on a Mettler-Toledo TGA/SDTA 851E instrument. A 12.757 mg sample of **1** was heated in nitrogen atmosphere at a heating rate of 5 °C min⁻¹.