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Synthesis and characterization of a new mixed-metal oxide framework material composed of vanadium oxide clusters: X-ray crystal structure of $(N_2H_5)_2[Zn_3V^{IV}{}_{12}V^{V}{}_6O_{42}(SO_4)(H_2O)_{12}]\cdot 24H_2O$

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The reaction of a slurry of V_2O_5 with $LiOH\cdot H_2O$ and hydrazinium sulfate gives a dark colored solution that upon treatment with $ZnSO_4\cdot 7H_2O$ yields the novel framework material $(N_2H_5)_2[Zn_3V^{IV}{}_{12}V^{V}{}_6O_{42}(SO_4)(H_2O)_{12}]\cdot 24H_2O$, composed of three-dimensional arrays of the mixed-valence $\{V_{18}O_{42}(SO_4)\}$ clusters interlinked *via* $\{Zn(H_2O)_4\}$ bridging groups, containing tunnels occupied by exchangeable cations and water molecules.

Polyoxovanadates constitute an important subclass of metal oxide clusters with an exceptional capacity to form mixed-valence compounds that exhibit rich electronic and magnetic properties and have relevance to catalysis, geochemical and biochemical processes, and in materials science.[1] Well characterized clusters containing four to 34 vanadium atoms – many with mixed-valence and coupled V^{IV}-centers, ranging from closed cages and spherical shells to basket, bowl, barrel, and belt shaped open structures are known.[2] Strikingly, their structures are related to, and in principle derived from, the appropriate V_2O_5 sheet fragments.[2] Given the significance of transition metal oxide surfaces[3] and proven roles of polyoxometalate clusters in catalysis,[4] it is conceivably rewarding to attempt to design and prepare transition metal oxide based materials (*e.g.* novel surfaces and zeolitic and layered solids) with desired and controllable properties by assembling metal oxide clusters of appropriate attributes. Through this communication we describe the synthesis and characterization of a novel framework material, composed of well defined vanadium oxide clusters, prepared under mild synthetic conditions.

The reaction of a stirring slurry of V_2O_5 (2.5 mmol) in water (25 mL) at 84–86 °C with $LiOH\cdot H_2O$ (5 mmol) and hydrazinium sulfate (2.5 mmol) gave a dark colored solution that upon treatment with $ZnSO_4\cdot 7H_2O$ (1.25 mmol) yielded prism-shaped dark crystals of $(N_2H_5)_2[Zn_3V^{IV}{}_{12}V^{V}{}_6O_{42}(SO_4)(H_2O)_{12}]\cdot 24H_2O$, **1**, in 12 h at room temperature in 65% yield (based on V). Besides the H_2O and hydrazine absorption bands, the IR spectrum (KBr Pellet) of **1** exhibits features at 1135m $\nu(SO_4)$], 989s [$\nu(V–O_{terminal})$] and 704m and 631m cm^{-1} [$\nu(V–(\mu_3\text{-}O)$)].

The extended highly symmetrical structure of **1**,[5] shown in Fig. 1, consists of three-dimensional arrays of $\{V_{18}O_{42}(SO_4)\}$ clusters each one connected to six other neighboring units *via* $\{Zn(H_2O)_4\}$ bridging groups. The building block units in the structure of **1**, shown in Fig. 2, consist of $\{V_{18}O_{42}(SO_4)\}$ clusters formed from the $\{V_{18}O_{42}\}$ shell[6] encapsulating a tetrahedral $\{SO_4\}^{2-}$ moiety with disordered oxygen atoms. The host shell, constructed from $18\{VO_5\}$ square pyramids sharing edges through 24 μ_3-oxygen atoms, behaves as a container for the $\{SO_4\}^{2-}$ group which is not an integral part of the shell. The guest $\{SO_4\}^{2-}$ group with normal S–O distances (1.472 Å) rattles inside the host shell. The square pyramidal geometry around each vanadium (V1) in twelve of the $18\{VO_5\}$ groups is defined by a terminal oxo group (O2) and four μ_3-oxygens (O1) of the shell. The geometry around vanadium (V2) in the remaining $6\{VO_5\}$ units is defined by four basal μ_3-oxo groups (O1) and an apical μ-oxygen (O3) which in turn is linearly bonded to the zinc(II) center of one of the six $\{Zn(H_2O)_4\}$ bridges, forming $\{V(2)–O(3)–Zn(H_2O)_4–O(3)–V(2)\}$ bonds, that link $\{V_{18}O_{42}(SO_4)\}$ clusters. The octahedral geometry around each zinc(II) is completed by four oxygen atoms (O4) from the aqua ligands, each one disordered over two positions, and two *trans*-μ-oxo (O3) groups.

The Zn(1)–O(4) distance (2.063 Å) and the bond valence sum (BVS)[7] value (0.36) identify O(4) oxygen as H_2O. This conclusion and the result of the manganometric titration of V^{IV} sites (12 V^{IV} per formula unit) requires two units of negative charge per $[Zn_3V^{IV}{}_{12}V^{V}{}_6O_{42}(SO_4)(H_2O)_{12}]$ unit which is balanced by the two $N_2H_5{}^+$ -hydrazinium cations. The cations and lattice waters (with disordered hydrogens) occupy the rectangular tunnels, defined by $\{V_{18}O_{42}(SO_4)\}$ and $\{Zn(H_2O)_4\}$ units, in the structure (Fig. 1). The cations are readily exchangeable by other cations ($NH_4{}^+$, Na^+, K^+, *etc.*) without noticeable change in the framework structure.

This report presents a new synthetic solid with three-dimensional structure composed of well defined vanadium oxide clusters held together without incorporating conventional ligands[8] in its structure. This underlines the potential of polyoxometalates in the design and development of well

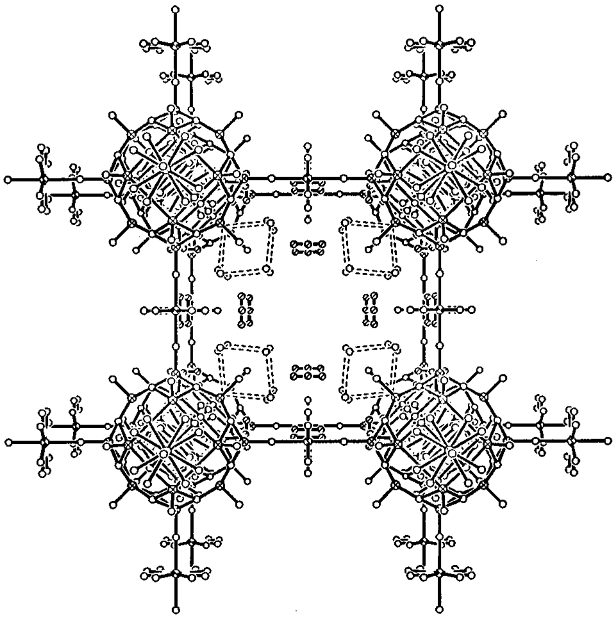

Fig. 1 View of the extended structure of $(N_2H_5)_2[Zn_3V^{IV}{}_{12}V^{V}{}_6O_{42}(SO_4)(H_2O)_{12}]\cdot 24H_2O$ showing interpenetrating nets of $\{V_{18}O_{42}(SO_4)\}$ clusters interconnected through $\{Zn(H_2O)_4\}$ bridging groups, and rectangular channels occupied by the hydrogen bonded water molecules (open circles) and hydrazinium ions (striped circles). Hydrogen atoms and the central cluster in the unit cell are not shown.

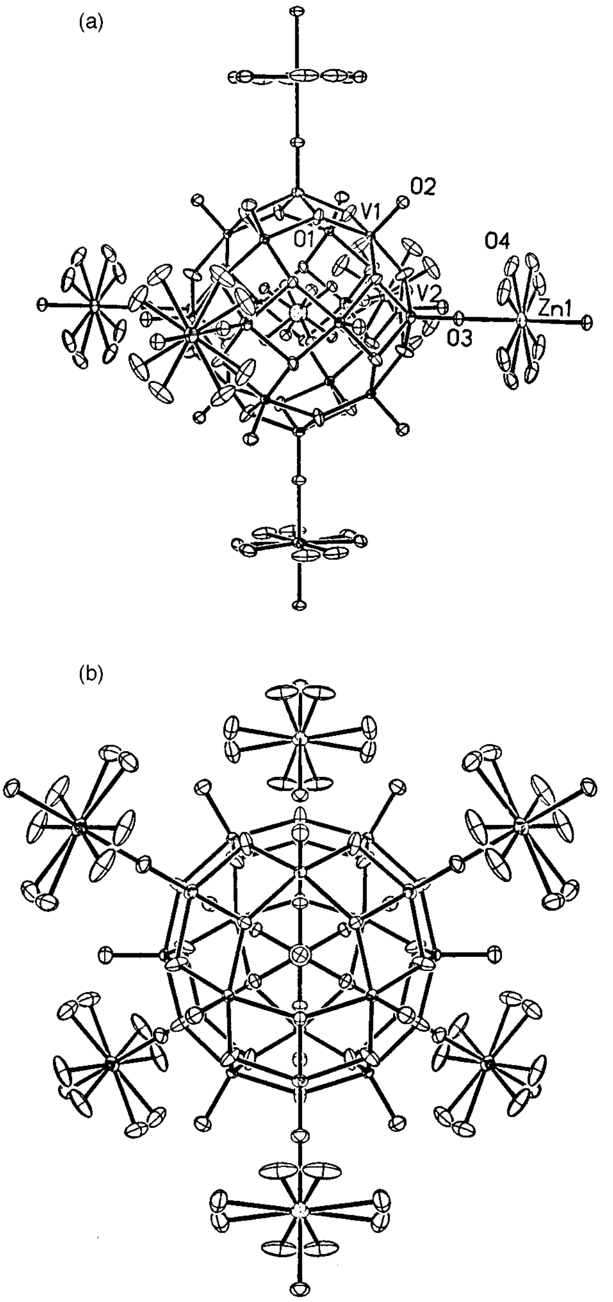

Fig. 2 (a) The building block units in the crystal structure of $(N_2H_5)_2[Zn_3V^{IV}_{12}V^{V}_6O_{42}(SO_4)(H_2O)_{12}]\cdot 24H_2O$ showing the atom labeling scheme in the asymmetric unit. (b) A view of the building unit along the threefold axis (hydrazinium ions and water molecules are omitted). Key: central circle with regular dot pattern represnts sulfur atom (S1); Atoms bonded to S1 represent O5 atoms. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): V(1)–O(2) 1.588, V(1)–O(1) 1.9515, V(2)–O(3) 1.634, V(2)–O(1) 1.953, Zn(1)–O(4)(H_2) 2.063, Zn(1)–O(3) 2.122, S(1)–O(5) 1.472, V(1)–V(2) 2.9441 Å.

characterizable solids whose properties could possibly be correlated with their constituent units. Besides their possible catalytic, ion exchange and sorbtive properties, currently under investigation in our labs, synthetic solids, like **1,** composed essentially of metal oxide fragments may provide a model for understanding the chemical transformations catalyzed by metal oxide surfaces.[9]

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