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Inorganic–organic hybrids derived from oxovanadium sulfate motifs: synthesis and characterization of $[V^{IV}O(\mu_3-SO_4)(2,2'-bpy)]_\infty$

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The hydrothermal reaction of V_2O_5 , V_2O_3 , 2,2'-bpy and Na_2SO_4 in dilute sulfuric acid yields a novel hybrid, $[V^{IV}O(\mu_3-SO_4)(2,2'-bpy)]_\infty$, which demonstrates the potential of constructing a new class of robust composite solids composed of a $\{V/O/SO_4\}$ -based framework decorated with organic functionalities by combining appropriate vanadyl sulfate motifs with a variety of organic ligands.

The amalgamation of oxovanadate moieties with the tetrahedral $\{PO_4\}$ ligand has produced an impressive array of vanadium–oxide–phosphate based systems with fascinating electronic and structural properties.^{1–8} Oxovanadiumphosphate-based porous-framework materials containing unprecedented large cavities and channels similar to those observed in conventional zeolites and solids with double-helix structure have been synthesized and characterized in recent years.^{7,8} As compared to the $V/O/PO_4$, however, well-defined $V/O/SO_4$ -based inorganic materials prepared from the combination of sulfate with oxovanadate units are rare.^{9–11}

Since vanadium exhibits extensive coordination chemistry involving a variety of organic ligands,¹² the solids constructed from $\{V/O/SO_4\}$ system may, in principle, incorporate appropriate organic ligands. This offers opportunity for making new inorganic–organic hybrid (composite) phases containing an inorganic $\{V/O/SO_4\}$ backbone decorated with organic functionalities. Such compounds are practically unknown.^{10d} We are currently exploring the potential of this approach¹³ which, to our knowledge, has not been exploited for materials design and development. This report describes the synthesis and characterization by IR spectroscopy, thermogravimetry, elemental analysis, manganometric titration, bond valence sum calculations, and complete single crystal X-ray structure analysis of a new solid $[V^{IV}O(\mu_3-SO_4)(2,2'-bpy)]_\infty$ **1**.

Green needle shaped crystals of **1** are prepared in ~78% yield by the hydrothermal reaction of V_2O_5 , V_2O_3 , Na_2SO_4 , 2,2'-bpy and 1 M H_2SO_4 in the molar ratio 0.5:0.5:5:3:10 at 180 °C for 48 h.[†]

The crystal structure[‡] of **1** is shown in Fig. 1. It may be viewed as constructed from the centrosymmetric dimer building block, $[V^{IV}_2O_2(\mu_3-SO_4)_2(2,2'-bpy)_2]$, which contains two $[V^{IV}O(\mu_3-SO_4)(2,2'-bpy)]$ units linked through sulfate groups. The crystal packing views, which exhibit alternating inorganic ($VOSO_4$) and organic (2,2'-bpy) layers, are aesthetically appealing. The extended structure consists of parallel running inorganic chains decorated by organic ligands. The individual chains contain $\{VO_4N_2\}$ octahedra and $\{SO_4\}$ tetrahedra joined by common vertices. Every sulfate ligand, which uses three oxygen atoms to bond three vanadium centers, bridges three $\{VO_4N_2\}$ octahedra each one of which, in turn, shares vertices with three $\{SO_4\}$ groups. This generates a series of eight-membered $\{-V-O-S-O-V-O-S-O-\}$ rings that are fused to construct the entire chain. The overall geometry around sulfur is a slightly distorted tetrahedron. All O–S–O angles (105.5–112.7°) and the S–O bond distances are in the normal range. The octahedral geometry around each vanadium center is

defined by a terminal oxo group, three μ -O groups from the three adjacent sulfate ligands in the chain, and two nitrogen donor atoms from a chelating 2,2'-bpy ligand. The terminal oxo groups on vanadium centers alternate such that any two adjacent vanadium atoms will have their terminal oxo groups pointing toward the opposite sides of the chain.

The structure and building block units in **1** are significantly different to those observed in our earlier reported compound $[V^{IV}_2O_2(OH)_2(\mu-SO_4)(2,2'-bpy)_2]$ **2**.^{13a} The structure of **2** consists of ribbons constructed from the infinite inorganic chains, $[-\{V_2O_2(\mu-OH)_2\}(\mu-SO_4)\{V_2O_2(\mu-OH)_2\}-SO_4]$, composed of pairs of edge sharing $\{VO_2(OH)_2N_2\}$ octahedra joined by $\{SO_4\}$ tetrahedra, laced by organic (2,2'-bpy) ligands. The metrical parameters of the two $V/O/SO_4/2,2'-bpy$ -based hybrid materials (**1** and **2**) are comparable.

The comparison of the two structures may suggest the possible transformation of **2** into **1** by the replacement of the two μ -OH groups in **2** by a μ_3-SO_4 group, cleavage of $\{V-(OH)-V\}$ bonds, and concomitant formation of new $\{V-(SO_4)-V\}$ bonds accompanied by condensation. So far, we have not achieved the chemical interconversion between **1** and **2**. Compound **1** can, however, be prepared by the slight modification in the reaction used to synthesize **2**. The structure of **1** is strikingly similar to a recently reported compound $[Fe^{III}_2Cl_2-(MoO_4)_2(2,2'-bpy)_2]$ **3**¹⁴ in which $\{FeCl\}$ and tetrahedral $\{MoO_4\}$ groups occupy the positions equivalent to that of $\{VO\}$ and $\{SO_4\}$ groups, respectively, in **1**. This suggests that $\{Fe^{III}Cl\}$ and $\{Mo^{VI}O_4\}$ groups are topologically equivalent to $\{V^{IV}O\}$ and $\{S^{VI}O_4\}$, respectively.^{15a}

The bond valence sum[§] calculations^{15b} and manganometric titration (of V^{IV} sites) results are consistent with the formulation and charge balance requirements of **1**. Thermogravimetric analysis of **1** reveals its remarkable thermal stability showing no weight loss up to ~420 °C, a two-step weight loss in the range 423–488 °C corresponding to the decomposition of 2,2'-bpy and sulfate ligands, and no further weight change up to 600 °C. The IR spectrum of the black residue exhibits features [at 994w, 738m br, 699(sh), 532m and 439m cm^{-1}] of a reduced vanadium oxide phase that has not been further characterized.

This report underlines the potential of the approach for making new and robust inorganic–organic hybrid phases. In view of the spectacular progress in the design and development of $V/O/PO_4$ -based materials, it is clear that many more $V/O/SO_4$ -based systems remain to be discovered. The suitable combination of oxovanadate sulfate fragments and organic ligands could yield new composites (and nanocomposites) that may exhibit properties unobserved in purely organic or inorganic phases.

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Notes and references

[†] A mixture of V_2O_5 , V_2O_3 , Na_2SO_4 , 2,2'-bpy and 1 M H_2SO_4 in molar ratio 0.5:0.5:5:3:10 contained in a 23 ml Teflon-lined Parr autoclave was

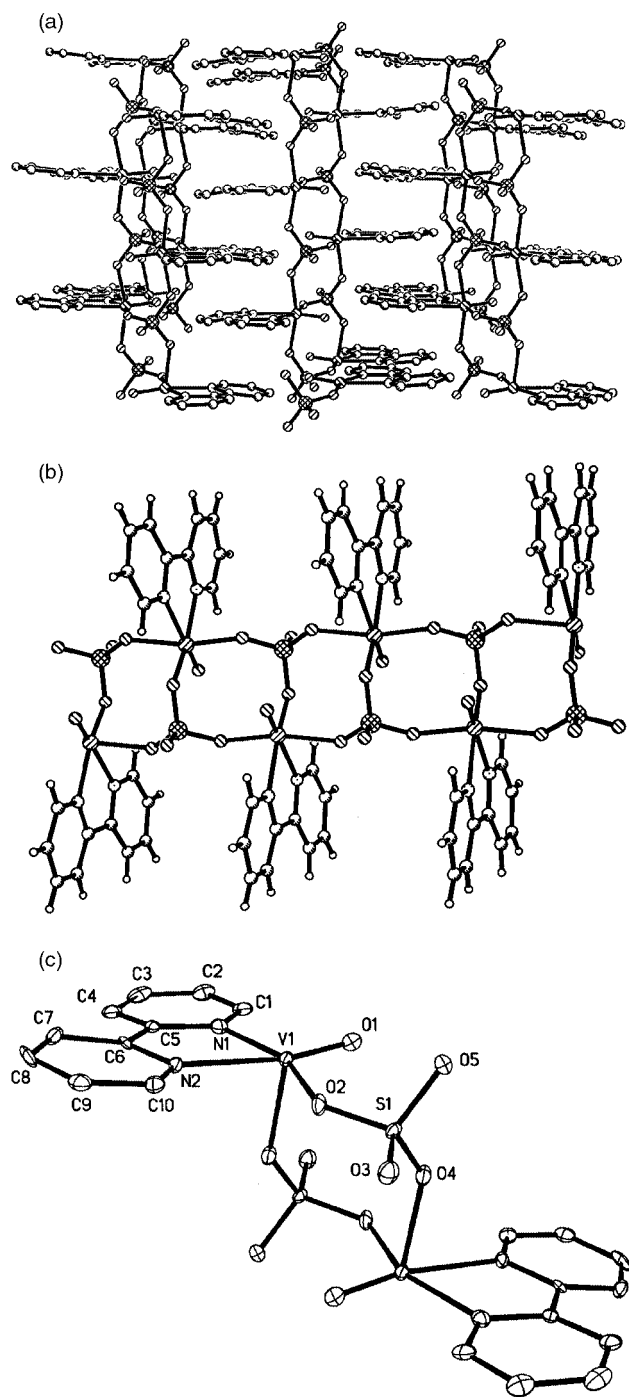


Fig. 1 (a) A view of the extended structure of $[V^{IV}O(\mu_3\text{-SO}_4)(2,2'\text{-bpy})]_\infty$. (b) Structure of a chain showing eight-membered rings. (c) The centrosymmetric building block unit in the crystal structure of **1** showing atom-labeling scheme. Hydrogen atoms are not shown. Selected bond lengths (\AA): V1–O1 1.582(5), V1–O2 1.994(5), V1–O4 2.046(5), V1–O5 2.062(5), V1–N1 2.1339(6), V1–N2 2.259(6), S1–O3 1.442(5), S1–O4 1.479(5), S1–O5 1.484(5), S1–O2 1.499(5).

heated for 48 h at 180 °C. After cooling the autoclave for 4 h, crystals of **1** were filtered from mother-liquor, washed with water, and dried in the air at

room temperature. The filtrate gave a second crop of **1**. Compound **1** could also be prepared by the hydrothermal reactions of $[VO(\text{H}_2\text{O})_4\text{SO}_4]\text{XSO}_4$ {X = $[\text{HN}(\text{C}_2\text{H}_4)_3\text{NH}]^{2+}$ or $[\text{H}_2\text{N}(\text{C}_2\text{H}_4)_2\text{NH}_2]^{2+}$ },^{13b,c} 2,2'-bpy, Na_2SO_4 and 2 M sulfuric acid in the molar ratio 1.25:5:2:10 at 180 °C for 48 h. Crystals of **1** are stable in air, insoluble in common solvents, and analyzed satisfactorily for C, H, N and S. *Selected IR absorption bands* for **1**: (KBr pellet, 1400–500 cm^{-1}): 1315m, 1250s, 1234s, 1158s, 1124s, 1112s, 1097s, 1056s, 1044s, 1030s, 1022s, 979s, 897w, 807w, 771s, 732s, 684m, 655m, 648w, 633m, 597s, 587s, 505m cm^{-1} .

‡ *Crystal data* for **1**: $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_5\text{SV}$, $M = 319.18$, monoclinic, space group $P2_1/n$, $a = 6.4102(6)$, $b = 16.4887(16)$, $c = 10.2176(10)$ \AA , $\beta = 99.417(2)^\circ$, $U = 1065.40(18)$ \AA^3 , $Z = 4$, $T = 158(2)$ K, $D_c = 1.99$ Mg m^{-3} , $\mu = 1.146$ mm^{-1} , $F(000) = 644$, crystal size = $0.22 \times 0.05 \times 0.03$ mm. A total of 7756 reflections ($2.37 \leq \theta \leq 23.27^\circ$) were collected, of which 1530 unique reflections were used for structural elucidation ($R_{\text{int}} = 0.0487$). The final $R1$ was 0.0658 (all data).

CCDC reference number 167561. See <http://www.rsc.org/suppdata/cc/b1/b106866k> for crystallographic data in CIF or other electronic format.

§ 4.0 valence unit per vanadium center in the compound.

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- (a) Shannon ionic radii (\AA): $\text{S}^{6+} = 0.29$; $\text{Mo}^{6+} = 0.59$; $\text{Fe}^{3+} = 0.55$ (low spin), 0.65 (high spin); $\text{V}^{4+} = 0.58$; $\text{Cl}^- = 1.81$; $\text{O}^{2-} = 1.40$ (R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751); (b) I. D. Brown, in *Structure and Bonding in Crystals*, ed. M. O'Keefe and A. Navrotsky, Academic Press, New York, 1981, vol. II, p. 1.