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Inorganic–organic hybrids derived from oxovanadium sulfate motifs: synthesis and characterization of $[\text{V}^{IV}\mu_3\text{SO}_4(2,2'\text{-bpy})]_x$

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The hydrothermal reaction of $\text{V}_2\text{O}_5$, $\text{V}_2\text{O}_3$, 2,2'-bpy and $\text{Na}_2\text{SO}_4$ in dilute sulfuric acid yields a novel hybrid, $[\text{V}^{IV}\mu_3\text{SO}_4(2,2'\text{-bpy})]_x$, 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 $\{\text{PO}_4\}$ ligand has produced an impressive array of vanadium–oxide–phosphate based systems with fascinating electronic and structural properties. The oxovanadiumphosphate-based porous-framework materials containing unprecedented large cavities and channels similar to those observed in conventional zeolites have been synthesized and characterized in recent years. As compared to the V/O/ SO$_4$ framework materials containing unprecedented large cavities, the octahedral geometry around each vanadium center is defined by a terminal oxo group, three $\mu$-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 $[\text{V}^{IV}_2\text{O}_5(\text{OH})_2(\mu_3\text{SO}_4)(2,2'\text{-bpy})]_x$. The structure of 2 consists of ribbons constructed from the infinite inorganic chains, $[-\{\text{V}_2\text{O}_5(\mu\text{-OH})(\mu_3\text{SO}_4)\}]_x$, composed of pairs of edge sharing $\{\text{VO}_2(\text{OH})_2\}$ octahedra joined by $\{\text{SO}_4\}$ tetrahedra, and two nitrogen donors from the 2,2'-bpy ligands. The geometrical 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 $\mu$-(OH) groups in 2 by a $\mu$-SO$_4$ group, cleavage of $[\text{V}^{IV}O(\text{OH})_2\text{SO}_4]$ bonds, and concomitant formation of new $[\text{V}O_2\text{SO}_4]$ 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$^{III}_2\text{Cl}_2(\text{MoO}_4)(2,2'\text{-bpy})]_3$ in which [FeCl] and tetrahedral $[\text{MoO}_4]$ groups occupy the positions equivalent to that of $[\text{VO}]$ and $[\text{SO}_4]$ groups, respectively, in 1. This suggests that [Fe$^{III}\text{Cl}$] and $[\text{MoV}_2\text{O}_7]$ groups are topologically equivalent to $[\text{V}^{IV}\text{O}]$ and $[\text{V}_2\text{O}_7]$ groups, respectively.

The bond valence sum calculations and manganometric titration of (VII) site 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 9944, 738m br, 699(sh), 532m and 439 m 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 $\text{V}_2\text{O}_5$, $\text{V}_2\text{O}_3$, $\text{Na}_2\text{SO}_4$, 2,2'-bpy and 1 M H$_2$SO$_4$ in molar ratio 0.5:0.5:5:3:10 contained in a 23 ml Teflon-lined Parr autoclave was
A view of the extended structure of [(VO(H2O)4SO4)XSO4] X = [HN(C6H4)2(NH)3] or [H2N(C6H4)2(NH)2]2. Structure of a chain showing eight-membered rings. (c) The centrosymmetric building block unit in the crystal structure of compound. The filtrate gave a second crop of crystals of I, stable in air, insoluble in common solvents, and analyzed satisfactorily for C, H, N and S. Selected IR absorption bands for I: (KBr pellet, 1400–500 cm⁻¹): 1315m, 1250s, 1234s, 1158s, 1124s, 1097s, 1056s, 1044s, 1030s, 1022s, 979s, 897w, 807w, 771s, 732s, 684m, 655m, 564w, 573w, 576s, 505m cm⁻¹. Crystal data for I: C24H24N9O13S4V, M = 319.18, monoclinic, space group P21/n, a = 6.4102(6), b = 16.4887(16), c = 10.2176(10) Å, β = 99.417(2)°, U = 1065.40(18) Å³, Z = 4. T = 150 K, D₂₅ = 1.99 Mg m⁻³, μ = 1.146 mm⁻¹, F(000) = 644, crystal size = 0.22 x 0.05 x 0.03 mm. A total of 7756 reflections (2.37 ° ≤ θ ≤ 23.27°) were collected, of which 1530 unique reflections were used for structural elucidation (R(int) = 0.0487). The final R1 was 0.0658 (all data).

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§ 4.0 valence unit per vanadium center in the compound.

15 (a) Shannon ionic radii (Å): Sr²⁺ = 0.29; Mo³⁺ = 0.59; Fe²⁺ = 0.55 (low spin), 0.65 (high spin); V⁴⁺ = 0.58; Cl⁻ = 1.81; O²⁻ = 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. Navařítky, Academic Press, New York, 1981, vol. II, p. 1.