Hydrothermal synthesis and structural characterization of a tubular oxovanadium organophosphonate, $(H_3O)[(V_3O_4)(H_2O)(PhPO_3)_3]\cdot xH_2O$ ($x = 2.33$)

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The hydrothermal reaction of KVO_3, $PhPO_3H_2$ and water at 180 °C for 116 h yields the tubular mixed valence V^V/V^{IV} polymer $(H_3O)[(V_3O_4)(H_2O)(PhPO_3)_3]\cdot xH_2O$ ($x = 2.33$).

The widespread contemporary interest in metal phosphonate materials[1–3] reflects their potential applications as sorbents, ion exchangers,[4] ionic conductors,[5] nonlinear optical materials,[6] sensors[7] and catalysts.[8] The vanadyl organophosphonate system has proved particularly fruitful and is represented by molecular clusters of various nuclearities, and one-, two- and three-dimensional phases.[9–11] In common with metal organophosphonates in general, lamellar structures predominate for the vanadyl organophosphonate subclass, with $[(VO)(H_2O)(PhPO_3)]$[12] providing the structural prototype. Lamellar vanadyl organophosphonates possess structurally well defined internal void spaces and coordination sites which allow intercalation of substrate molecules. Modifications of organic substituents, introduction of templating reagents, and variations in metal–phosphonate compositions can be exploited to change substrate-specific recognition and to design novel phases. It is also apparent that variations in reaction conditions can result in significant structural reorganization.[13–15] Thus, the novel tubular material $(H_3O)[(V_3O_4)(H_2O)(PhPO_3)_3]\cdot xH_2O$ **1** (x = 2.33) was prepared by relatively minor modification of the synthetic procedure employed in the isolation of the lamellar $[(VO)(H_2O)(PhPO_3)]$.[12]

The reaction of MVO_3 ($M = NH_4^+, Na^+, K^+$), $PhPO_3H_2$ and water in the mole ratio 1 : 2.33 : 340 at 180 °C for 116 h yielded dark green hexagonal rods of $(H_3O)[(V_3O_4)(H_2O)(PhPO_3)_3]\cdot xH_2O$ **1** (x = 2.33)† in 75% yield. Although the inorganic cation of the vanadate starting material does not appear in the product, it is absolutely required for the synthesis of **1**, an observation which highlights the often critical role of sacrificial cations in hydrothermal synthesis. Consequently, the reaction of V_2O_5 with $PhPO_3H_2$ under identical conditions yields only $[VO(H_2O)(PhPO_3)]$. It is noteworthy that hydrothermal treatment of $[VO(H_2O)(PhPO_3)]$ with Na^+ at pH 2 results in quantitative conversion to **1**. However, compound **1** was not isolated in more basic environments, where an undefinable powder was observed to form. Attempts to prepare **1** from oxovanadium phenylphosphonate clusters such as $[V_5O_7(OMe)_2(PhPO_3)_5]^-$,[16] and Na^+ in nonaqueous solvents proved fruitless. However, such clusters proved perfectly adequate for synthesis under hydrothermal conditions, suggesting that a solvent of a high dielectric constant is required and that the synthesis of **1** occurs through disassembly of oxovanadium phosphonate units rather than fusion of discrete clusters or unzipping of layered structures into infinite chains which subsequently fuse into the tubular form.

As illustrated in Fig. 1, the structure of **1**‡ consists of $[(V_3O_4)(H_2O)(PhPO_3)_3]_n^{n-}$ tubes running parallel to the c-axis. The phenyl groups extend outward from the periphery of the tube, while the vanadyl oxo groups are directed both to the interior and exterior of the cavity. The hydronium cation and the water molecules are contained within the hydrophilic interior of the tube, while the phenyl groups of the tube interdigitate with phenyl groups from adjacent tubes to provide a hydrophobic exterior.

The walls of the tube are constructed from three independent oxovanadium centers, an aqua group and three phosphonate bridging ligands, shown in Fig. 2. Two of the vanadium sites

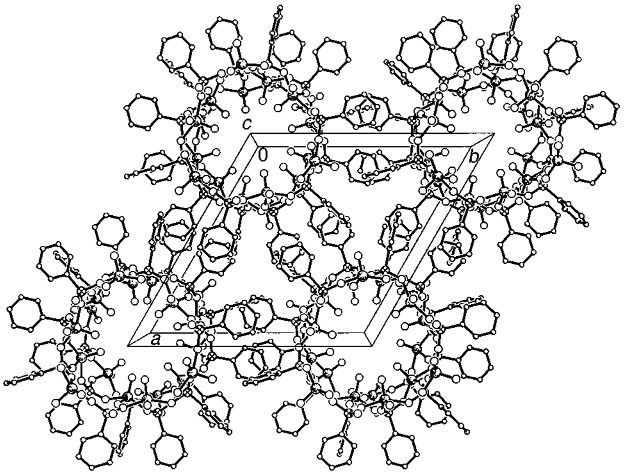

Fig. 1 A view along the crystallographic c axis of the tubular structure of the anions of **1**. The hydronium cations and water molecules of crystallization occupy the hydrophilic interior of the tube. The phenyl groups project outward from the tubes and interdigitate in the hydrophobic domains outside the tubes.

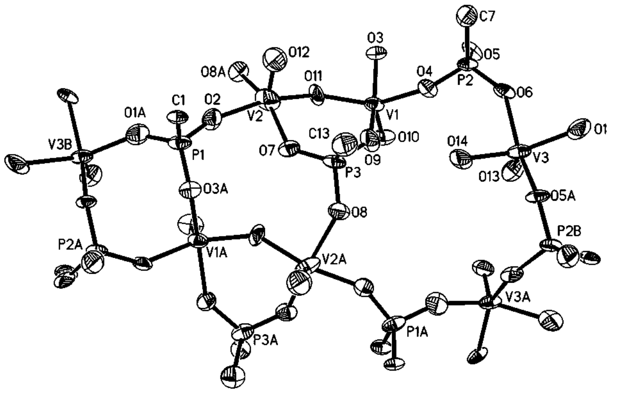

Fig. 2 A view of the V–O–P building blocks of the tube walls, showing the atom-labeling scheme and 50% probability ellipsoids. Selected bond lengths (Å): V1–O10 1.563(3), V1–O11 1.928(3), V1–O3 1.946(3), V1–O9 1.974(3), V1–O4 1.979(3), V2–O12 1.621(4), V2–O11 1.880(3), V2–O7 1.905(3), V2–O2 1.929(3), V2–O8 1.987(3), V3–O13 1.596(4), V3–O5 1.902(3), V3–O6 1.955(3), V3–O1 1.970(4), V3–O14 2.005(4).

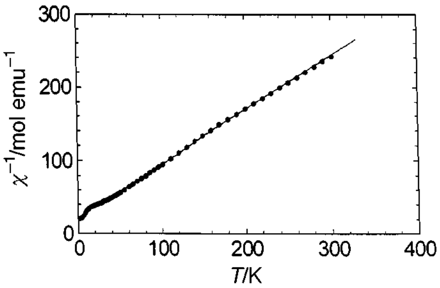

Fig. 3 A plot of $1/\chi$ *vs.* temperature, showing the Curie fit to the data

form a binuclear unit of corner-sharing square pyramids with the terminal oxo-groups in *anti*-orientation with respect to the V–O–V bridge. The remaining three coordination sites on each vanadium center are occupied by oxygen donors from the phosphonate ligands. The third vanadium site V3 is an isolated square pyramid (no V–O–V interactions). The oxo-group is directed toward the interior of the tube, while the coordinated aqua ligand forms parts of the tube wall. The complex pattern of phosphonate bridging of metal centers provides four distinct heteronuclear ring motifs as fundamental building blocks[18] of the tube wall: six atom (VOVOPO), eight atom $(VOPO)_2$, ten atom (VOVOPOVOPO) and sixteen atom $(VOPO)_4$ cycles.

The temperature dependence of the magnetic susceptibility of **1** is shown in Fig. 3. Above 40 K, the magnetic susceptibility conforms to the Curie–Weiss law with a Curie constant corresponding to 3.27 μ_B and a Θ value of -27 K. The effective moment for each of two V^{IV} ions is 2.33 μ_B, indicating a significant orbital contribution to the moment as anticipated for the $^2T_{2g}$ ground state. The negative Θ value indicates the presence of antiferromagnetic spin interactions, and the deviation from Curie–Weiss behavior below 40 K can be ascribed to the coupling of the spins of the d^1 V^{IV} sites. These observations are consistent with charge balance and valence sum calculations[17] which give an average oxidation state of 4.33 per vanadium site, or 1 V^V and 2 V^{IV} centers.

Thermogravimetric analysis of **1** shows weight losses corresponding to 1 and *ca.* 1.5 water molecules of crystallization at 50–60 and 120–140 °C, respectively. A weight loss corresponding to two additional water molecules occurs between 245 and 275 °C. The material decomposes sharply at 305 °C with an additional 30% weight loss to produce a blue amorphous material.

While **1** represents the first example of a tubular structure for the vanadium–organophosphonate system, tubular uranyl phosphonates have been reported recently.[13–15] However, the structure of the wall of **1** is quite distinct from the uranyl species which do not form U–O–U bonds. When viewed down the tube axis, the structure of **1** presents the circular projection also observed for $(UO_2)(PhPO_3)\cdot 0.7H_2O$, whereas $[(UO_2)_3(PhPO_3H)_2]\cdot H_2O$ exhibits a rectangular profile. Although the uranyl materials exhibit neutral tubes, the tube in **1** is anionic with charge compensation provided by hydroxonium cations, which occupy the interior of the tube and hydrogen bond to oxo-groups of the tube wall and water molecules which stuff the tube interior. Furthermore, the vanadyl sites of **1** are five coordinate, a geometry achieved through coordination to terminal and bridging oxo-groups and η^3,μ_3-phosphonate ligation. In contrast, the uranyl centers of the circular tubular material $(UO_2)(PhPO_3)\cdot 0.7H_2O$ are seven coordinate, exhibiting the common *trans* dioxo unit and requiring that the phosphonate adopt the η^3, μ_5-coordination mode. The structure of **1** exhibits two of the phenomena that critically influence the organization of organic–inorganic composite materials, namely, multipoint hydrogen bonding and hydrophilic–hydrophobic interactions.[18]

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Notes and References

† The value of 2.33 for the water of crystallization was estimated from elemental analyses, TGA (*vide infra*) and refinement of the population parameters of the water oxygen atoms in the X-ray crystal structure refinement.

‡ *Crystal data* for $C_{18}H_{24.67}O_{17.33}P_3V_3$ **1**; $P\bar{3}$, a = 18.6754(4), c = 13.8500(4) Å, V = 4183.3(2) Å^3, Z = 6, D_c = 1.820 g cm^{-3}; solution and refinement based on 4932 independent reflections converged at $R1$ = 0.0582, $wR2$ = 0.1627. CCDC 182/986.

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