The crystal structure of hexakis(2-(pyridin-2-ylamino)pyridin-1-ium) decavanadate(V) dihydrate, C_{60}H_{64}N_{18}O_{30}V_{10}

Table 1: Data collection and handling.

| Crystal: Orange block | Size: 0.21 × 0.20 × 0.18 mm |
| Wavelength: Mo Kα radiation (0.71073 Å) | μ: 1.28 mm⁻¹ |
| Diffractometer, scan mode: Bruker SMART APEX II, ϕ and ω | R_{max}, completeness: 25.0°, >99% |
| N(hkl)_{measured}, N(hkl)_{unique}, R_{int}: 36474, 6612, 0.100 | Criterion for I_{obs}, N(hkl)_{gt}: I_{obs} > 2 σ(I_{obs}), 3700 |
| N(param)_{refined}: 532 | Programs: Bruker [1], SHELX [2] |

Source of material

In a 50 ml round-bottom flask, dipyridylamine (0.513 g; 3 mmol), vanadium pentoxide (0.730 g; 4 mmol) and tetramethylammonium hydroxide 25% in solution (1.461 g; 4 mmol) were added successively to 20 ml water and acetic acid. The mixture was stirred for 24 h and then heated to 60 °C for 1 h, resulting in an orange coloured solution. The resulting mixture was filtrated and the filtrate stood for seven days. Crystals of the title compound suited for X-ray diffraction were obtained.

Yield: 38%, and elemental analysis: calc. for C_{60}H_{64}N_{18}O_{30}V_{10}: C 35.56, H 3.18, N 12.44; found: C 35.52, H 3.23, N 12.36. The elemental analyses were performed with PERKIN ELMER MODEL 2400 SERIES II.

Experimental details

In the title compound all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned with common isotropic displacement factors U_iso(H) = 1.2 times U_eq(C, pyridine ring; O, water molecule; N, pyridine ring and secondary amine). All the H atoms were refined as riding on their parent atom.

Comment

Polyoxovanadates, as an outstanding large important branch of anionic metal-oxo clusters, have led to a rapid
growth due to their structural features and promising applications in diverse areas, such as catalysis, electricity, medicine and functional materials [3–6]. The design and synthesis of new polyoxovanadates architectures with well-defined structures expand the range of polyoxovanadates-inspired hybrid materials [7, 8]. Thus, a lot of hybrid polyoxovanadates have been presented [9]. In addition, as a class of versatile tridentate N-ligands, dipyriddyldiamine (dpa) can be used in the synthesis of metal complexes, and some of them have been reported [10, 11]. Nevertheless, to the best of our knowledge, examples of dpa-based polyoxovanadates are still rare.

The structure of title hybrid dipyriddyldiaminepolyoxovanadates is shown in the figure. Single crystal diffraction analysis of the title compound revealed that it
consists of six protonated dipyrindylamine ligands, one decavanadate ployanion cluster and two free lattice water molecules, formulated as (Hdpa)\textsubscript{6}\text{V}_{10}\text{O}_{28}\cdot2\text{H}_{2}\text{O}. For the polyanion, the decavanadate cluster is composed of ten analogous VO\textsubscript{6} units, which bridged by edge- and corner-sharing oxygen atoms and each vanadium atom of VO\textsubscript{6} subunit exhibited the distorted octahedral geometry, located around a center of inversion. There are four distinct types of oxygen coordination, namely terminal O\textsubscript{t}, bridging μ\textsubscript{3}-O, μ\textsubscript{1}-O and μ\textsubscript{2}-O oxygen atoms. The bond lengths and angles found in the decavanadate anion are as expected for those in the previously reported decavanadate structures [12–14]. Each dpa ligand has a protonated hydrogen atom on the nitrogen of pyridinyl moiety. The C–N bond average distance in the pyridine ring of dpa ligands is 1.351 Å, which is larger than that of the unprotonated pyridine.

In addition, the supramolecular structure of the title structure was stabilized by intermolecular electrostatic interactions and strong hydrogen-bonding interactions between V\textsubscript{10}O\textsubscript{28}\textsuperscript{5-}, Hdpa\textsuperscript{1-} subunits and water molecules. All subunits are connected to the adjacent ones through various intermolecular C–H···O, N–H···O and O–H···O hydrogen-bonding interaction, thus leading to a three-dimensional network.

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