Hydrate von Li_3VO_4: Synthese und Strukturchemie

Hydrates of Li_3VO_4: Synthesis and Structural Chemistry

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Stoichiometric hydrates of Li_3VO_4, the hexahydrate and two polymorphs of the octahydrate, were prepared by evaporation of alkaline aqueous solutions 1 molar in LiOH and 0.5 molar in the metavanadate $LiVO_3$ at r. t. with or without the addition of Lithium sulfide, *i. e.* at different pH values. Their crystal structures have been determined and refined using single crystal X-ray data; all lithium and hydrogen atom positions were localised and refined without contraints.

All three title compounds crystallise in non-centrosymmetric space groups. The water molecules belong to the tetrahedral coordination spheres of the Li cations, *i. e.* they are embedded as water of coordination exclusively. The tetrahedral orthovanadate(V) anions VO_4^{3-} and the LiO_4 tetrahedra are connected *via* common O corners to form building units which are further held together by strong, nearly linear hydrogen bonds.

The hexahydrate $Li_3VO_4 \cdot 6H_2O$ (space group $R3$, a = 962.9(2), c = 869.2(2) pm, Z = 3, $R1$ = 0.0260) contains isolated orthovanadate(V) anions VO_4^{3-} surrounded by a 3D network of corner-sharing $Li(H_2O)_4$ tetrahedra forming rings of three, seven and eight units. The water molecules are 'isolated' in the sense that no hydrogen bonds are formed between water molecules.

The octahydrate is dimorphous: The triclinic polymorph of $Li_3VO_4 \cdot 8H_2O$ (space group $P1$, a = 592.6(2), b = 651.3(2), c = 730.2(4) pm, α = 89.09(2), β = 89.43(2), γ = 88.968(12)°, Z = 1, $R1$ = 0.0325) contains two types of chains of tetrahedra: One consists of corner-sharing $Li(H_2O)_4$ tetrahedra only, the second one is formed by alternating LiO_4 and VO_4 tetrahedra, also sharing oxygen corners. Only one water molecule is 'isolated', the other seven form a branched fragment of a chain with hydrogen bonds between them.

In the monoclinic form of $Li_3VO_4 \cdot 8H_2O$ (space group Pc, a = 732.6(1), b = 653.7(1), c = 1292.9(3) pm, β = 112.21(1)°, Z = 2, $R1$ = 0.0289) a fragment of a chain of three LiO_4 tetrahedra, two of which share a common edge, and one VO_4 tetrahedron represent the formular unit. These building blocks are connected *via* hydrogen bonds formed by three 'isolated' water molecules and a chain fragment of five connected water molecules.

Key words: Vanadates, Lithium, Hydrates