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Structure Of [(Hoc₂h₄)₃nh]₄P₄O₁₂ R. Nahouane^a, E. H. Soumhi^a, I. Saadoune^a and A. Driss^b

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Organic-cation phosphates have been intensively studied due to their many uses in various fields such as protonic conductors and nonlinear optics [1-2]. Most organic-cation phosphates are formed essentially in the way of H-bond between phosphoric anions and organic groups which contain generally donor centers [3-4]. In the present paper, we report detailed structural investigation of a new organic-cation cyclotetraphosphate obtained by using a tertiary amine: (HO-CH₂-CH₂)₃N. The compound was prepared by neutralization of H₄P₄O₁₂ with organic amine in a 4:1 molar ratio. The H₄P₄O₁₂ solution was prepared using an aqueous solution of Na₄P₄O₁₂ and an ion-exchange resin (Amberlite IR-120). Colorless single crystals appeared after evaporation of the solution at room temperature for a few days. The compound has been studied by single crystal X-ray diffraction. The crystals belong to space group P2₁/n with unit cell parameters: a = 9.945(2) Å, b = 14.591(3) Å, c = 14.428(3) Å and β = 101.12(2)°. The asymmetric unit of the title compound consists of two triethanolammonium cations and two PO₄ tetrahedra which form one half of a P₄O₁₂ cycle built around an inversion centre. All bond distance and angle values deduced from the refinement are in good agreement with those observed in similar condensed phosphates [3-4]. From a general point of view, the structure of this phosphate could be described as a succession of two types of layers parallel to (-1 0 1) plane. The first one formed simultaneously by the (P₄O₁₂)⁴⁻ anions and the second organic cation (N2). The second layer is formed only by the first organic cation (N1). The hydrogen bonds contribute significantly to stabilizing the structure of this salt.

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Structural Changes upon Lithium insertion in Co_{0.5}TiOPO₄ Rachid Essehli^{a,b}, Brahim El Bali^a, Helmut Ehrenberg^{b,c}, Ingrid Svoboda^b, Kristian. Nikolowski^b, Natalia Bramnik^b and Hartmut Fuess^b ^aLaboratory of

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Recently, we discovered a new class of lithium insertion compounds by investigating the ternary diagram of (MO-TiO₂-P₂O₅). These oxyphosphates M_{0.5}TiOPO₄ (M = Co²⁺, Ni²⁺, Cr²⁺...) could act as electrodes for lithium batteries that provide high energy density. Up to three lithium atoms could be inserted per crystalline cell generating thus an initial practical capacity of 434 mAh/g. The structural investigation of the phase transformations occurring upon lithium insertion in Co_{0.5}TiOPO₄, for the two ex-situ diffraction pattern were taken for the composition of and Li₃Co_{0.5}TiOPO₄. For Li₃Co_{0.5}Ti^{III}OPO₄ the amorphization of the sample was observed. The LiCo_{0.5}TiOPO₄ structure has been determined from conventional X-ray powder diffraction data, by Rietveld method in P2₁/c space group. The cell parameters are: [a = 7.3385(1)Å, b = 7.6066(1)Å, c = 7.5507(1)Å, β = 118.75(2)° and Z = 4]. This structure can be described as a 3-dimensional network of [TiO₆]-, [LiO₆]- and [CoO₆]-octahedra and [PO₄] tetrahedra. LiO₆ and CoO₆ octahedra share edges and form chains running parallel to the a axis. Each PO₄ tetrahedra shares 2 oxygen atoms with two TiO₆ consecutive octahedra of one chain and one oxygen atom with a neighboring parallel chain of the sheet. Links of sheets by the remaining oxygen atom of phosphate tetrahedron lead to a [TiOPO₄]^{III} three-dimensional framework. Titanium atoms are displaced from the geometrical center of the octahedra resulting in long (2.303(1) Å) Ti-O(5) and short (1.613(1) Å) Ti-O(3). The four remaining are between 1.839(1) and 2.149(1) Å distances. In one chain the off-center displacement of Ti atoms induces creation of electric moments. As the space group P2₁/c is centrosymmetric, there is compensation of antiparallel moments of an adjacent chain, so LiCo_{0.5}Ti^{III}OPO₄ is antiferroelectric

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