The (3+1)-dimensional superspace description of an incommensurately modulated organic zwitterion dehydrate with solvent disorder

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The structure of a dihydrate of (3S)-2-(4-azaneyl)-3-hydroxy-3-methyl-1-(11-oxidaneyl)-4-phenoxybutan-1-one (1), which is a zwitterion of (3S)-2-amino-3-hydroxy-3-methyl-4-phenoxybutanoic acid is presented in three and (3+1)-dimensional space. The 100 K incommensurately modulated structure is refined based on the main and first order satellite reflections in superspace group \( P2_12_12_1(0 \beta 0)000 \) and \( q \) vector component \( \beta = 0.357 \). The structure is modulated in the 100–298 K range. Whereas the satellite reflections are well observed, a single-crystal approximation that disregards them produces a high-quality structure both with spherical and aspherical atomic form factors. Attempts to solve and refine the structure in the supercell with the \( b \) axis tripled were unfruitful. A theoretically optimized geometry of (1) at the B3LYP/6-311+G(d,p) level of theory is in excellent agreement with the single-crystal structure, RMSD = 0.123 Å for non-H atoms. The absolute structure and absolute configuration were unambiguously established by resonance scattering effects despite the Friedel = 30.64.

There is an extensive hydrogen-bonding network formed by neutral and charge-assisted N–H...O and O–H...O interactions in the crystal. The hydrogen-bonded layers and aromatic layers are parallel to the crystallographic \((110)\) plane and alternate in the \([001]\) direction. One of the solvent water molecules is disordered over two positions in a ~2:1 ratio; these molecules exhibit the most pronounced atomic displacive modulations described with a crenel function. The hydrogen-bonding patterns formed by these partially occupied molecules change along the fourth dimension, and this competition among the different H-bonding interactions is believed to be the reason for the modulation. Alternative approaches to refining the (3+1)-dimensional structure are discussed.

Figure 1. Electron density plots showing the atomic motion of the partially occupied water molecule oxygen atoms O6 (66.5(4) %) and O7 (33.5(4) %) along \( x_1 \) (left) and occupational modulation along \( x_2 \) (middle, right) as a function of \( x_4 \). For all plots, the electron density is summed over a thickness of 1 Å in the remaining directions. Solid and dashed black lines indicate areas of positive and negative electron density. The colored lines represent the crenel functions used to model the occupancy modulation and paths of motion of the O6 (red) and O7 (blue) atoms as a function of \( x_4 \). This modulation is manifested in a positionally disordered water molecule that is split over the O6 and O7 sites.