

[o.m3.p1] The true symmetry of $[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3]_2[\text{FeO}(\text{PO}_4)_4] \cdot \text{H}_2\text{O}$ with an open-framework structure.

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In the literature¹ the structure of the title compound is described as a framework build from iron oxide phosphate. The cubane-like building units Fe_4OPO_4 possess the $-43m$ symmetry due to interchange of Fe and P in the corners of the "cube" connected via oxygen bridges. The peculiarity of the structure is the linking of the building units exclusively through the corners so that between the cubes there are large voids filled by a template ethylenediamine. A tetragonal unit cell ($a=10.1383(8)$, $c=9.628(1)$ Å) and the space group $I-43m$ were proposed. The structure was determined by single crystal x-ray diffraction and the authors reported difficulties with the crystals which exhibited very nice forms but the reflections were broad, having several maxima, and many crystals had to be tested before finding one that gave the unit cell. Also the final R values were quite high ($R=0.077$, $R_w=0.065$).

A similar compound was prepared by hydrothermal synthesis and the x-ray powder pattern indicated a different structure. The first attempt to determine the structure using single crystal x-ray diffraction was unsuccessful due to very broad reflections with several overlapping maxima. It was not even possible to determine the unit cell, however, it was quite clear that the nice-looking crystals are in fact multiples.

The problem was then solved using well resolved powder pattern from a laboratory diffractometer. Comparison of the observed powder pattern with the calculated one (using the published structure¹) showed that the structures must be related, just the compound from our analysis had lower symmetry. The actual unit cell was found to be monoclinic ($a=10.087(1)$, $b=10.109(1)$, $c=9.638(1)$ Å, $\beta=91.688(5)^\circ$), reduction of the symmetry then led to the space group $I2$.

The formation of multiples due to small deviations of the true monoclinic structure from the more symmetric tetragonal is understandable. The published tetragonal structure is in fact the average over the multiple orientations of the monoclinic domains. This was proven by the Rietveld refinement which was conducted to elucidate the nature and reasons of the small deviations of the actual structure from the tetragonal average.

[1] DeBord J.R.D., Reiff W.M., Warren C.J., Haushalter R.C., Zubieta J. "A 3-D Organically Templated Mixed Valence ($\text{Fe}^{2+}/\text{Fe}^{3+}$) Iron Phosphate with Oxide-Centered $\text{Fe}_4\text{O}(\text{PO}_4)_4$ Cubes: Hydrothermal Synthesis, Crystal Structure, Magnetic Susceptibility, and Mossbauer Spectroscopy of $[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3]_2[\text{FeO}(\text{PO}_4)_4] \cdot \text{H}_2\text{O}$ ", Chem. Mater., (1997), 9: 1994-1998.

[o.m3.p2] The structure and dynamics of doubly occupied Ar hydrate.

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Clathrate hydrates are non-stoichiometric compounds with a host framework formed by hydrogen bonded water molecules and enclathrated gas molecules. The crystal structure of clathrate hydrate is known as Stackelberg's structure I or II¹ depending on the gas molecule size though the structure H was found in 1987. Recently, it has been suggested that the large cages of type II structure have the capability of encaging with double guest molecules.²

In this study molecular dynamics (MD) simulations of Ar-hydrate have been performed with variable cage occupancy by Ar atoms. The MD calculations were done with 1088 water molecules and 8 to 256 Ar atoms using the KKY potential model³. The simulation temperature was kept at 80K. The stability of clathrate hydrate affected by Ar double occupancy in the large cavities was examined by both constant volume (NVT) and constant pressure (NPT) calculations.

In a series of MD calculations both pressure and total energy were found to increase when the large cavities were doubly occupied. The radial distribution function (RDF) was calculated to investigate the distribution of Ar atoms in the cages. In the doubly occupied large cages a sharp Ar-Ar RDF peak was located at 3.3Å for Ar atoms in the same cage. Power spectra of Ar atoms with the cage occupancy S16L0, S16L8 and S16L16⁴ were calculated via velocity autocorrelation functions. The spectrum of Ar atoms in the small cages was found at 50 cm^{-1} in all occupancy. In contrast, the spectrum of Ar atoms in the large cages is a single peak at 17 cm^{-1} for single occupancy (S16L8), and becomes double peaks at 25 and 42 cm^{-1} for double occupancy (S16L16).

[1] von Stackelberg M. and Muller H. R. "On the structure of gas hydrates.", Z. Elektrochem., (1954), 58: 25-39.

[2] Kuhs W. F., Chazallon B., Radaelli P. G. and Pauer F. "Cage occupancy and compressibility of deuterated N2-clathrate hydrate by neutron diffraction.", J. Incl. Phenom., (1997), 29: 65-77.

[3] Kumagai N., Kawamura K. and Yokokawa Y. "An interatomic potential model for H_2O : Applications to water and ice polymorphs.", Mol. Simul., (1994), 12: 177-186.

[4] S is the occupancy of the small cages and L is the occupancy of the large cages. For example, S16L8 means 16 Ar atoms for small cages occupied and 8 Ar atoms for large cages.