MS30-1-3 Structural variability of MOFs built from a tetratopic phosphinate ligand
#MS30-1-3

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Abstract
Metal organic frameworks (MOFs) using phosphinate ligands showed recently to be stable even under hydrothermal conditions [1]. Mixing ligand tricyclo[3.3.1.1^{3,7}]decane-1,3,5,7-tetrayltetrakis(phenyl-4-methylphosphinic acid (H_4TPATP(Me), Figure 1A) with ferric ions led to formation of three different phases. The major phase (ICR-11, space group *P*-3, a=24.3(1), c=9.50(5)Å) has significant proton conductivity because two out of four phosphinate groups are not coordinated to iron but form walls of the channels running parallel along *c* direction [2]. 3D electron diffraction (3D ED) experiments revealed two more minor phases. One has triclinic Bravais lattice and shows low level of crystallinity, which demonstrates itself in diffuse scattering features. The other phase is monoclinic (space group *C*2/*c*, a=15.48(1), b=29.03(1), c=23.75(1) Å, beta=91.1(1)°) and the structure was solved ab initio (Figure 1B). The iron cations form trimers interconnected by six phosphinate groups. Two other phosphinate groups are capping the terminal iron cations from both sides leading to eight coordinated phosphinate groups in total However, the three ferric ions have nine positive charges. This results in one positive charge per trimer, which is compensated by formic acid, which has only about 0.5 occupancy at both ends of the trimer. Even though the structure is very large (nearly 11000 Å^3), it was possible to perform dynamical refinement [3], which clearly revealed the position of the half-occupied carbon atom of the coordinated formic acid. The unit cell contains 488 non-hydrogen atoms, which makes it the largest dynamically refined structure.
Acknowledgement:
We thank Czech Science Foundation (project no. 20-04408S) for financial support.

References
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Figure 1 Tetratopic phosphinate ligand H4TPATP(Me)