

[1] S.N. Britvin, S.V. Krivovichev, W. Depmeier, O.I. Siidra, D.V. Spiridonova, V.V. Gurzhiy, A.A. Zolotarev, *PCT Patent Application PCT/EP2010/001864* filed March 25, 2010.

**Keywords:** layered titanates, adsorption, reduction

## MS.25.4

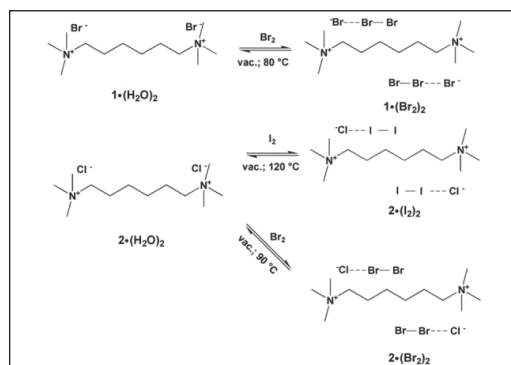
*Acta Cryst.* (2011) A67, C69

### Solid-State synthesis of mixed trihalides via reversible absorption of dihalogens by non porous onium salts

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1,6-Bis(trimethylammonium)hexane bis(trihalides)  $1\cdot(\text{Br}_2)_2$  and mixed bis(trihalides)  $2\cdot(\text{I}_2)_2$  and  $2\cdot(\text{Br}_2)_2$  have been synthesized by treating the corresponding dihydrated halides  $1\cdot(\text{H}_2\text{O})_2$  and  $2\cdot(\text{H}_2\text{O})_2$  with molecular dihalogens (e.g.,  $\text{Br}_2$  and  $\text{I}_2$ ) under gas-solid and solution conditions (Figure 1).[1] Despite the fact that the starting hexamethonium halides are non porous, the trihalides syntheses occur homogeneously, in quantitative yields, and reversibly. In all the cases the halogen bond [2] prevails over the hydrogen bond, and the hydrogen bonded water in the starting material is substituted by the halogen bonded dihalogens to form the crystalline trihalides. The stability of the trihalides is mainly due to cooperative halogen bond and cation templation effect [3]. Hexamethonium halides are proven effective solids for the clathration and storage of molecular dihalogens. While the starting salts are not isostructural, all the formed trihalides and mixed trihalides are isostructural. Single crystal X-ray diffraction, powder X-ray diffraction and Raman experiments have confirmed the formation of the solid trihalides. The method we describe is general and can be extended to the preparation of various uncommon trihalides species like interconversion of trihalides and mixed trihalides via solid-gas processes.

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**Figure 1.** Synthesis of the complexes  $1\cdot(\text{Br}_2)_2$ ,  $2\cdot(\text{I}_2)_2$  and  $2\cdot(\text{Br}_2)_2$  via reversible gas-solid reactions and their reversion to  $1\cdot(\text{H}_2\text{O})_2$  and  $2\cdot(\text{H}_2\text{O})_2$ .

**Keywords:** gas-solid reactions, non porous salts, inclusion

## MS.25.5

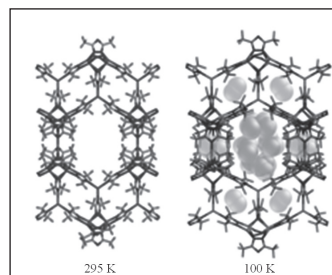
*Acta Cryst.* (2011) A67, C69

### Experimental visualization of breathing in fluorinated metal-organic frameworks from single crystal diffraction - functionalized MOFs for gas storage and separation

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Fluorinated metal-organic frameworks (FMOFs) are a new class of advanced porous material with fluorine-lined pore surface and hydrogen-free. Reaction of silver(I) and 3,5-bis(trifluoromethyl)-1,2,4-triazolate in toluene/acetonitrile yields FMOF-1, the first example in the FMOF family, that shows high-density gas uptake and unique hysteretic sorption of  $\text{H}_2$  [1]. Variable single crystal X-ray diffraction measurements reveals that FMOF-1 undergoes remarkable breathing and negative thermal expansion when the crystal is exposed to  $\text{N}_2$  at ambient pressure [2]. Upon cooling a apparent negative thermal expansion takes place with very large changes in volume and unit-cell parameters during which multiple  $\text{N}_2$  molecules are absorbed into channels and cages (see picture).

Details of the dynamic gas adsorption mechanism at the atomic level will be presented to illustrate the functional control and sequential filling of the multiple gas adsorption sites in both small and large pores within FMOF-1 and the consequent remarkable swelling of these framework cavities. Real-time 3D reciprocal space mapping technique employed at the SNS TOPAZ beam line for the analyses of guest-host interaction and structural transformation in MOFs will be introduced.



Work at ORNL was supported by UT-Battelle, LLC, under contract No. DE-AC05-00OR22725 with the US Department of Energy.

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**Keywords:** gas storage, neutron diffraction, metal-organic framework

## MS.26.1

*Acta Cryst.* (2011) A67, C69-C70

### Understanding hydrogenation properties of various hydrogen storage materials from their local structure

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