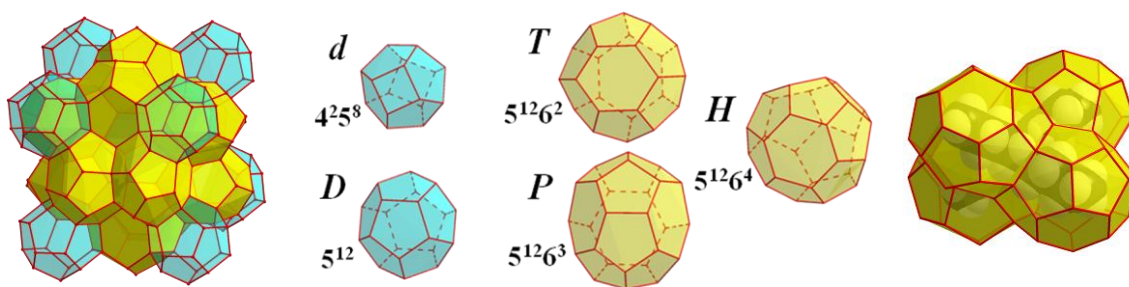


STRUCTURE OF IONIC CLATHRATE HYDRATES OF TETRABUTYL- AND TETRAISOAMYLAMMONIUM HALOGENIDES

*Manakov A.Yu., Komarov V.Yu., Rodionova T.V., Grachev E.V.,
Terekhova I.S., Solodovnikov S.F., Podoksenov A.V.
Nikolaev Institute of Inorganic Chemistry SB RAS,
3, Acad. Lavrentieva avenue, Novosibirsk, 630090, Russian Federation
komarov_v_y@ngs.ru*

Ionic clathrate hydrates (*ICH*) of tetrabutyl- and tetraisoamylammonium (*TBA*, *TiAA*) salts are classical objects of inclusion chemistry. Almost from the moment they were discovered, their comprehensive study has attracted^{1,2} and continues to attract³⁻⁸ attention because of their fundamental importance as well as some applications.

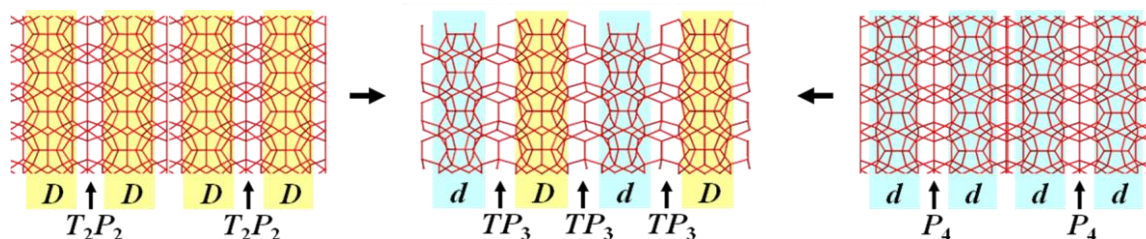


From left to right: a fragment of a host framework, small (*d*, *D*) and large (*T*, *P*, *H*) cavities, *TBA* cation included into a four-compartment cavity

The host frameworks of these *ICH* can be described as four-connected networks (idealized gas hydrate-like networks) which contain defects. Two main types of defects are (1) replacement of a water molecule by an anion and (2) vacancy existence resulting in the formation of combined cavities (*CC*). Within the existing concepts of *TBA* and *TiAA* halogenides *ICH* crystal chemistry, anions substitute an equivalent quantity of water molecules, forming hydrogen bonds with four adjacent host framework molecules (hydrophilic inclusion with tetrahedral coordination); guest cations are located in four-compartment *CC* (hydrophobic inclusion); every large cavity (*T*, *P*) of the idealized framework must be involved in *CC* formation, while small cavities (*d*, *D*) may be presented as individual ones in *ICH* host framework and remain unoccupied. Formation of several *ICH* phases with the differing composition in the *TBA* (*TiAA*) salt — H₂O systems is attributed to the difference of their idealized framework types.

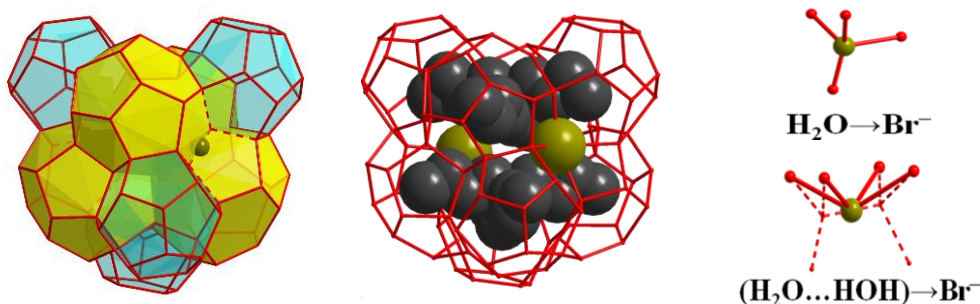
Theoretical and experimental investigations of title compounds carried out by our research group have yield some results which have been extending knowledge about structure of these *ICH*. Some of the most interesting results are listed further.

- Systematical enumeration of four-connected polyhedral (zeolite-like) networks within some constrained classes has been performed. Constrains used were caused by structural features of the clathrate hydrates. E.g. 29 simplest networks were obtained that are tilings which contain less than eight different *D*, *T*, *P* and *H* polyhedral-based tiles in the fundamental domain.



Formation of hybrid host framework type of *TiAAI ICH* (in center) from parent ones.

- The crystal structure of *TiAAI ICH* with previously unknown idealized host framework has been obtained. This framework which is described as a hybrid of two early known ones demonstrated the possibility of homologous series formation.



An eight-compartment D_4T_4 CC and the types of Br^- coordination were found in *TBABr ICH*.

- Investigation of *TBABr ICH* has revealed formation of eight-compartment CC which contained pairs of *TBA* cations. Unusual non-planar square coordination of halogenide-ion also was found in this structure. Formation of a number of *ICH* phases having the same idealized host framework type in *TBABr* — H_2O and *TBACl* — H_2O systems was demonstrated.
- Formation of polymorphs differed solely in mutual orientation of CC was found for *TiAABr ICH*. X-ray diffuse scattering patterns point that the CC and guest cations in these crystals have short-range order but lack more or less of long-range order.

The data obtained allow to extend the structural interpretation of *ICH* phase variety and reconsider some hypothesis previously assumed.

Financial support from Russian Foundation of Basic Research (Grant 09-03-00367) and Integration project №62 of SB RAS are gratefully acknowledged.

1. Dyadin Yu. A., Udachin K. A. *J. Struct. Chem.* **28**, 394 (1987)
2. Jeffrey G. A. *Comprehensive Supramolecular Chemistry* **6** (23), 757(1996)
3. Komarov V. Yu., Solodovnikov S. F., et al *Crystallography Reviews* **13** (4), 257 (2007)
4. Arjmandi M., Chapoy A., et al *J. Chem. Eng. Data* **52**, 2153 (2007)
5. Soldatov D. V., Suwińska K., et al *J. Struct. Chem.* **49** (4), 712 (2008)
6. Shin K., Kim Y., et al *J. Phys. Chem., A* **113**, 6415 (2009)
7. Rodionova T. V., Komarov V. Yu., et al *J. Phys. Chem., B* **114** (36), 11838 (2010)
8. Manakov A. Yu., Rodionova T. V., et al *Proc. of the ICGH* Edinburgh, UK, July 17-21 (2011)