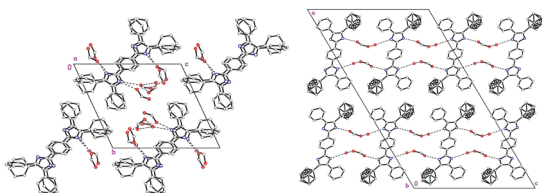


## FA4-MS31-P11

**Supramolecular associations in bisimidazole derivative/formic acid solvates.** L. Izotova<sup>(2)</sup>, J. Ashurov<sup>(2)</sup>, S. Talipov<sup>(2)</sup>, B. Ibragimov<sup>(2)</sup>, E. Weber<sup>(1)</sup>, <sup>1</sup>*Institute für Organische Chemie, TU Bergakademie Freiberg, Germany.* <sup>2</sup>*Institute of Bioorganic Chemistry, Tashkent, Uzbekistan*  
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Recently, heterocyclic imidazole derivatives (especially phenylimidazoles) have attracted considerable attention because of their unique optical properties [1]. From solution of formic acid have been obtained two types solvates of 1,4-bis(4',5'-diphenylimidazol-2-yl)benzene with formic acid – unstable and stable forms. The first unstable form – yellow plate, Sp.gr.P-1, cell parameters:  $a=10.420(2)\text{\AA}$   $b=13.804(3)\text{\AA}$ ,  $c=15.251(3)\text{\AA}$ ,  $\alpha=63.86(3)^\circ$ ,  $\beta=82.23(3)^\circ$ ,  $\gamma=70.58(3)^\circ$ ,  $V=1857.1(7)\text{\AA}^3$ , the host/guest ratio is 1:5. Five formic acid molecules form the glue between two molecules of bisimidazole derivative through hydrogen bonding, thus forming 0D supramolecular arrangement. The second stable form –yellow bulk needles, crystallized in C2/c space group and have following cell parameters:  $a=35.395(7)\text{\AA}$ ,  $b=5.1576(10)\text{\AA}$ ,  $c=20.607(4)\text{\AA}$ ,  $\beta=120.85(3)^\circ$ ,  $V=3229.7(11)\text{\AA}^3$ . Host/guest ratio is 1:2:2H<sub>2</sub>O. In this structure host and guest molecules *via* H-bonds are associated in 1D chain in the *c*-axis direction. A proton from the formic acid was transferred to one of the imidazole rings. Therefore one nitrogen of the imidazole ring is positively charged.



[1] P.T. Chou, M.L. Martinez, *Radiat. Phys. Chem.* 41 (1993) 373.

**Key words:** crystal engineering, hydrogen bonding, supramolecular assemblies

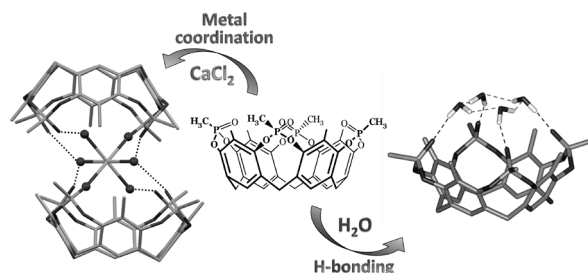
## FA4-MS31-P12

**Interplay between H-bonding and Metal Coordination in Tetrphosphonate Cavitands.** Chiara Massera<sup>a</sup>, Monica Melegari<sup>b</sup>, Enrico Dalcanale<sup>b</sup>, Franco Ugozzoli<sup>a</sup>, <sup>a</sup>*Department of General and Inorganic Chemistry, University of Parma, Italy,* <sup>b</sup>*Department of Industrial and Organic Chemistry, University of Parma, Italy*  
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Phosphorylated cavitands are an emerging class of versatile synthetic receptors, whose complexation properties span from neutral molecules like alcohols to positively charged species like ammonium and pyridinium salts [1]. In all these cases the molecular recognition phenomena depend on the synergistic effect of a  $\pi$ -basic cavity and of P=O groups at the upper rim which are effective H-bond acceptors. Here we report an innovative approach to the generation of a single tetrameric

water cluster in the solid state by using the tetrphosphonate cavitand template Tiiii[H<sub>2</sub>CH<sub>3</sub>,CH<sub>3</sub>].

The specific H-bond interaction pattern induced by the host *via* its rigidly preorganized four P=O acceptor groups leads to the exclusive formation of a cyclic water tetramer of C<sub>4</sub> symmetry [2]. The four P=O units form an array of H-bonding with the cluster, controlling the orientation of the free hydrogens below the molecular plane of the tetramer. This water cluster is maintained also if competitive alcoholic guests like methanol or ethylene glycol are added to the crystallization mixture. Considering the affinity of this class of receptors towards cationic species and water, we have decided to investigate their behavior in the presence of both components.



The rigidity and the preorganized geometry of the organic hosts are ideal to discriminate the differences in size and coordination propensity of metallic cations and thus to control the formation of the corresponding organometallic complexes. Three novel dimeric capsules formed by Tiiii[H<sub>2</sub>CH<sub>3</sub>,CH<sub>3</sub>] with barium, calcium and zinc salts have been synthesized and structurally characterized [3]. The role of cation dimensions and of coordinated water molecules in determining different architectures is also described.

[1] (a) Melegari M., Suman M., Pirondini L., Moiani D., Massera C., Ugozzoli F., Kalenius E., Vainiotalo P., Mulatier J.-C., Dutasta J.-P., Dalcanale E., *Chem. Eur. J.*, 2008, 14, 5772; (b) Biavardi E., Favazza, M., Motta A., Fragalà I.L., Massera C., Prodi L., Montalti M., Melegari M., Condorelli G.G., Dalcanale E., *J. Am. Chem. Soc.*, 2009, 131, 7447. [2] Massera C., Melegari M., Ugozzoli F., Dalcanale E., *Chem. Commun.*, 2010, 46, 88. [3] Melegari M., Massera C., Ugozzoli F., Dalcanale E., *Cryst. Eng. Comm.*, 2010, submitted.

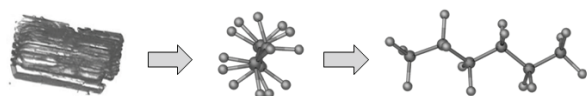
**Keywords:** Cavitands, Metal coordination, H-bonding

## FA4-MS31-P13

**Disorder in Self-assembled Halogen-bonded Perfluoroalkyl Onium Salts.** Tullio Pilati<sup>a</sup>, Antonio Abate<sup>b</sup>, Gabriella Cavallo<sup>b</sup>, Pierangelo Metrangolo<sup>b,c</sup>, Giuseppe Resnati<sup>a,b,c</sup>, Giancarlo Terraneo<sup>b,c</sup>, <sup>a</sup>*C.N.R. - I.S.T.M., University of Milan, Via C. Golgi 19, 20133 Milan, Italy,* <sup>b</sup>*NFMLab - D.C.M.I.C. "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131 Milan, Ital,* <sup>c</sup>*CNST - IIT@POLIMI, Politecnico di Milano, Via G. Pascoli 70/3, 20133 Milan, Italy*  
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In the last decade new families of liquid-crystalline materials based on non-covalent interactions such as hydrogen bonding, quadrupolar and charge-transfer interactions have been developed. Halogen bonding, namely any noncovalent interactions involving halogens as electrophilic species [1], has proven successful in driving self-assembly processes in supramolecular chemistry, crystal engineering, and materials

science [2]. We have used this interaction to realise the self-assembly of new families of liquid-crystalline materials based on perfluoroalkyl onium salts. An accurate choice of the starting components allowed us to produce superfluorinated ionic liquid crystalline materials with relatively high clearing points; some of those gave crystals of sufficiently good quality to be studied by single crystal X-ray diffraction. These compounds present an extensive disorder, mainly in the perfluorinated chains. In this contribution we present how to model the disorder, essential for a reasonable refinement of the structure, and which choices have driven our hands in selecting a good crystal for data collection. They are normally 'buttery' or at least very easily deformable, or extremely thin, or curved, twinned and often undergo phase transition at low temperatures.



[1] P. Metrangolo, G. Resnati, *Science* 2008, 321, 918. [2] P. Metrangolo, F. Meyer, T. Pilati, G. Resnati, G. Terraneo, *Angew. Chem. Int. Ed.* 2008, 47, 6114.

**Keywords:** Perfluoroalkyl Chains, Liquid Crystals, Disorder Modelling

#### FA4-MS31-P14

**Synthesis and Crystal structure of Diethyltin bis-dihydrogenphosphate, (Et<sub>2</sub>Sn)(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>** *Martin Reichelt<sup>a</sup>, Hans Reuter<sup>a</sup>,*  
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The title compound was synthesized from Et<sub>2</sub>SnO and H<sub>3</sub>PO<sub>4</sub>. Its colourless needle shaped crystals crystallise in the monoclinic space group C2/c (no. 15) with  $a = 22.4786(8)$  Å,  $b = 9.9382(3)$  Å,  $c = 20.3812(7)$  Å,  $\beta = 96.922(2)^\circ$ ,  $V = 4519.9(3)$  Å<sup>3</sup>,  $Z = 16$  and  $d = 2.180$  g/cm<sup>3</sup>. For structure solution and refinement 82153 reflections in the  $\theta$ -range 2.01°–28.00° were collected, resulting in 5450 unique reflections ( $R_{int} = 0.0396$ ) after applying an empirical absorption correction ( $T_{min} = 0.6360$ ,  $T_{max} = 0.8309$ ). In summary 286 parameters (2 restraints) were refined to  $R1 = 0.0212$ ,  $wR2 = 0.0453$  for 5450 reflections with  $I > 2\sigma(I)$  and  $R1 = 0.0252$ ,  $wR2 = 0.0465$  for all reflections.

The asymmetric unit consists of two formula units and contains {Et<sub>2</sub>SnO<sub>3</sub>} trigonal bipyramids and {PO<sub>4</sub>} tetrahedra, which are connected with each other to rings and chains. Via hydrogen bonds an extended three-dimensional framework is built up with channels parallel to the crystallographic b axis filled by the organic groups.

**Keywords:** tin compounds, phosphates, organic-inorganic hybrid materials

#### FA4-MS31-P15

**The crystal structure of  $\alpha$ -sodium stearate NaC<sub>18</sub>H<sub>35</sub>O<sub>2</sub> · 0.5 H<sub>2</sub>O.** *Alexandra Christine Schaap, Walter Frank, Institut für Anorganische Chemie und*

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Sodium soaps are materials with a wide range of industrial applications for example as detergents, greases, lubricants and cosmetics. Hence, the knowledge of the structural behaviour of sodium soaps is of general interest. However, until today crystallography of neutral sodium soaps is restricted to the determination of unit cell parameters [1, 2, 3, 4, 5]. Here we present the results of the first crystal structure determination of a curd soap,  $\alpha$ -sodium soap: NaC<sub>18</sub>H<sub>35</sub>O<sub>2</sub> · 0.5 H<sub>2</sub>O (**1**). Extremely thin platelet crystals of **1** were obtained by slow cooling of a propylglycolic solution that contained 5% of water. Soap **1** crystallizes in the triclinic space group  $P\bar{1}$  with unit cell parameters of  $a = 7.847(2)$  Å,  $b = 9.302(2)$  Å,  $c = 51.100(10)$  Å,  $\alpha = 91.68(3)^\circ$ ,  $\beta = 92.46(3)^\circ$  and  $\gamma = 90.11(3)^\circ$  and with  $Z = 2$ . The sodium soap can be described as a bilayered structure with a strict separation of hydrophobic and hydrophilic parts that can be considered as an arrangement of model membranes.

[1] Buerger, M.J., Smith L.B., de Bretteville, A., Ryer, F.V., *Proc. Natl. Acad. Sci. USA*, 1942, 28, 526. [2] Buerger, M.J., *Proc. Natl. Acad. Sci. USA*, 1942, 28, 529. [3] Buerger, M.J., Smith L.B., Ryer, F.V., Spike, J.E., *Proc. Natl. Acad. Sci. USA*, 1945, 31, 226. [4] Buerger, M.J., *Am. Mineral.*, 1945, 30, 551. [5] Minor, J.E., Lingafelter, E.C., *J. Am. Chem. Soc.* 1949, 71, 1145.

**Keywords:** soap,  $\alpha$ -sodium stearate, crystal structure determination

#### FA4-MS31-P16

**Engineering Metal Organic Frameworks with a Triazole-Tetrazole Ligand.** *Bernard Tinant<sup>a</sup>, Anil D. Naik<sup>b</sup>, Mathieu Monaux<sup>a</sup>, Yann Garcia<sup>a</sup>, <sup>a</sup>Institut de la Matière Condensée et des Nanosciences, Université Catholique de Louvain, Belgium*  
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Cavernous solids at the designer's aspiration have found applications in separation science, gas storage technology, sensors, catalysis, drug delivery [1]. In continuation of our modular approach to functional materials of metal-organic frameworks, [2] we now direct our interest to the coordination chemistry of a novel asymmetric tecton (L1H = (5-(4H-1,2,4-triazol-yl)-2H-tetrazole), whose crystal structure was solved. This molecule was designed based on a conceivable transamination method [3] and actually represents the first molecular tecton wherein two flagged motifs of 1,2,4-triazole and tetrazole were brought on the same platform in a conciliation conformation. This unique molecule can behave as bifunctional bridging ligand as well as anion. [Zn(phen)<sub>2</sub>(L1)]BF<sub>4</sub> (**1**) crystallises in a centrosymmetric space group (Pnma) with unsymmetrical L1 acting as 'interpolating' pillars and chelating phen as a capping ligand of hexa-coordinated Zn<sup>II</sup> ions thus affording a robust 2D zig-zag network propagated by  $\pi$ - $\pi$  interactions from heterocycles. The inclusion complex [Zn(bpy)<sub>3</sub>]<sub>2</sub>(L1) · (BF<sub>4</sub>)<sub>3</sub> · 10H<sub>2</sub>O (**2**) crystallises in a non-centrosymmetric space group (P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>). It is a mononuclear octahedral complex presenting trapped L1 molecules in the water occupied channels by multiple secondary interactions also acting as an anion. TGA-DTA of **1**