

FA4-MS10-P01**Topological Analysis of MOFs with Entanglements of 2-Periodic Structural Groups.**

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273 metal-organic frameworks (MOF) with entanglements of two-periodic structural groups (layers) were found by a comprehensive analysis of the Cambridge Structural Database using the program package TOPOS [1]. 163 Parallel and 108 inclined catenated layers were observed and in only in one case both modes of entanglement are realized together. TOPOS tools were applied to consider simplified representations of the structural groups as nets, where the nodes correspond to metals and/or centers of gravity of polydentate ligands. The most widespread type of topology of the layers in the simplified nets is the square net 44-sql (161 compounds); 65 MOFs have the topology of the honeycomb net 66-hcb; the third place is occupied by the topology 4.82-fes (13 cases). A strong correlation was found between the coordination type of ligand, the coordination number of central atom and the global topology of the net. Thus, in 146 compounds with the underlying topology of the square net, metal is connected to four bridge ligands. Out of them, in 122 compounds all the bridge ligands are bidentate, and in 83 compounds metal has coordination number six being connected to four bidentate-bridge and two monodentate dangled ligands. Among the compounds with the honeycomb type of topology the most frequent local topology is formed by three bidentate-bridge and two bidentate terminal (coordination number of metal is seven). It was shown, that the results obtained can be used to design the crystals containing tangled two-periodic structural groups.

Keywords: topology; entanglement; metal-organic frameworks

FA4-MS10-P02**Local and Global Topology of Two-Dimensional Structural Groups.**

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The analysis of local and global topology of two-dimensional metal-organic frameworks (MOF) in the crystal structures of 1303 coordination compounds of zinc, cadmium, copper and silver was made with the program package TOPOS (<http://www.topos.ssu.samara.ru>) [1]. 198 different types of global topologies (2D nets) were found, with the most frequent topology corresponding to square net 4⁴-sql (39,5%), followed by honeycomb net 6³-hcb (16,9%) and 4.8²-fes (7%).

The most widespread (12%) local topology of metal centers conforms to the coordination of two bidentate bridge and two monodentate terminal ligands, moreover, almost in all such cases (95%) they result in the 4⁴-sql global topology. Thus, in two-dimensional MOFs the topology of coordination centers severely determines the global topology of the net. At the same time, a given global topology can correspond to a number of local topologies to be distinguished by denticity of the ligands. We propose a general classification for these nets, where polyatomic ligands are contracted into unstructured centers of a new simplified net keeping the connectivity of the initial net. As a result, various methods of coordination of complexing atoms can be described within the same topological type of the simplified net and related to its global topology.

We have discussed the capabilities of this approach to predict the topological motifs in coordination polymers at the specified complexing atoms and ligands with a given denticity.

[1] Blatov V.A., *IUCr CompComm Newsletter*, 2006, 7, 4.

Keywords: topological aspects of structure; classification of crystal structures; computer analysis

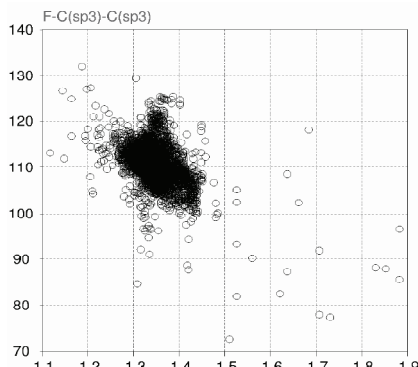
FA4-MS10-P03**Fluorine and Crystals Disorder.**

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Fluorine atoms are typically located at the periphery of organic molecules and, when bonded to neutral groups, are characterized by very weak intermolecular interactions with any kind of atom. Consequently, perfluorocarbon derivatives (PFCs) have lower boiling point compared with hydrocarbons having comparable molecular weight and very low friction coefficient; they are also hydrophobic and lipophobic and are poorly miscible with many organic solvents. Partially fluorinated molecules show similar trends as a function of the number of fluorine atoms. Weak intermolecular interactions mean crystallization problems, too. Plastic phases, liquid crystals, amorphous glasses and structural disorder are common in fluorinated compounds. Long PFCs show steric hindrance between fluorine atoms bonded in position 1,3 on the carbon chains; their stable conformation is then helical, distorted *all-trans*, with a pitch of 27-30 C-C bonds; near always the two enantiomeric helices are found in the same crystallographic site as disordered groups. The present work will show how common this disorder is and how frequently it is ignored, also in molecules with small fluorinated residues such as -CF₃. Asking for X-CF₃ (X any atom) under the conditions *No error, Not polymer, No ions, No powder structures*, we found 8752 hits from CCDC (version November, 2008); they became 6117 with *No disorder* and 3204 also with

$R \leq 0.05$. In spite of this restraints, the following scattergram shows that the dispersion of F-C distances and F-C-F angles is very broad, indicating that, in a large number of cases, disorder was possibly present but ignored by the authors. As a conclusion same typical cases of disorder will be discussed.



Keywords: weak interactions; analysis of disordered structures; fluorine compounds

FA4-MS10-P04

Absolute Configuration Determination: Is There More Information in the Data? David J. Watkin^a, Amber L. Thompson^a. ^a*Chemical Crystallography, Department of Inorganic Chemistry, Oxford.*

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A sample of unknown enantiopurity can be regarded as containing a mole fraction of a given hand equivalent to $1-x$, and x mole fraction of the other. Because the Flack x parameter [1] is a parameter in the refinement, its standard uncertainty $u(x)$ can also be determined giving a measure of the confidence in the assignment of the absolute structure. Flack & Bernardinelli [2] give confidence intervals for the assignment of the absolute structure of materials of new samples: For a sample of unknown enantiopurity, the value of $u(x)$ must be less than about 0.04 for x to be a reliable assignment of the chirality of the major component. If the material is known to be enantiopure, then the condition on $u(x)$ can be relaxed to 0.10 and x in the range 0.3 to -0.3 would be considered as confirming the stated configuration.

Increasingly, there has been a suspicion that these conditions are over-cautious. By examining the distribution of the Friedel differences, Hooft et al. [3] have derived a parameter, y , which lies in the interval 0 to 1 and behaves something like the Flack x parameter. Because the calculation is working with distributions, there is the possibility of estimating the probability, for a known enantiopure material, that the assigned hand is correct. Hooft et al. remark, "These probabilities can be surprisingly decisive, even when the resonant scattering signal is very weak".

Examination of the Flack x and the Hooft y parameters for the natural product, epiallexine (below) raised some interesting questions [4]. In order to get a snap-shot of the performance of the Flack and Hooft parameters, 120 recent data sets collected on known enantiopure light atom

materials measured using molybdenum radiation [5] have been examined and results will be presented.

[1] Flack H.D. **1983**. *Acta Cryst.*, A39, 876-881. [2] Flack H.D. & Bernardinelli G. **2000**. *J. Appl. Cryst.*, 33, 1143-1148. [3] Hooft, R.W.W., Straver, L.H. & Spek A.L. **2008**. *J. Appl. Cryst.*, 41, 1, 96-103. [4] Thompson, A.L., Watkin, D.J., Gal, Z.A., Jones, L., Hollinshead, J., Jenkinson, S.F., Fleet G.W.F. & Nash R.J. **2008**. *Acta Cryst.*, C64, o649-o652. [5] Thompson A.L. & Watkin, D.J., *Tet. Asym.*, in press.

Keywords: absolute configuration determination; chirality; small-molecule crystallography

FA4-MS10-P05

The Coordination Mode of the Carboxylate Ligands in Copper Complexes. Goran A. Bogdanović^a, Sladjana B. Novaković^a. ^a*VINČA Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter Physics, P.O. Box 522, 11001 Belgrade, Serbia.*

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Oxygen atoms from the carboxylate group possess four free electron pairs what enables the formation of different coordination modes with different number of metal atoms. Over 5000 crystal structures of copper complexes with carboxylate ligands have been analyzed using the Cambridge Structural Database (CSD) [1]. We have performed the classification of Cu carboxylate complexes based on geometrical parameters and frequency of structural motifs related to different coordination modes. The majority of crystal structures extracted from CSD can be described by two structural motifs: a) the carboxylate group is a part of chelate ring (five- or six-membered) with one carboxyl oxygen coordinated to the Cu atom, b) the carboxylate group is a bridging ligand connecting two Cu atoms. The second group of crystal structures has been analyzed in more details using different geometrical parameters. We found some preferential Cu...Cu interatomic distances related to different coordination modes of the carboxylate group.

[1] Allen F.H., *Acta Crystallogr.*, **2002**, B58, 380.

Keywords: Cambridge structural database; chemistry of complex compounds; carboxylates

FA4-MS10-P06

Conformational Analysis of Bidentate Tetra-Aryl Diphosphines. Claire L. McMullin^a, Natalie Fey^a, A. Guy Orpen^a. ^a*Department of Chemistry, University of Bristol, UK.*

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Phosphine ligands play an important role in many homogeneous catalytic reactions, including hydroformylation and asymmetric hydrogenation. In particular, bidentate tetra-aryl-substituted diphosphines allow fine-tuning of catalyst properties by modification