

this time and its creative energies not by piles of reprints nor lists of citations, but by the visually attractive fruits of our labors.

From the earliest times, as crystallographers searched for ways to depict and explain their structural results, clusters and juxtapositions of atoms have taken on striking artistic forms. This mini-symposium and the accompanying exposition of contemporary art are dedicated to the presentation of the aesthetic aspects of structural studies.

From the ephemeral refresh rate of the computer terminal to the durability of a wooden or metal sculpture, these images and forms are a stimulation to the scientist first seeing them, who then manipulates parameters to create forms and images that rise above the ordinary to magnify aesthetic images of nature from the atomic and molecular scale. The artist in us aspires [1] to create images and sculptures of lasting value. The support of the US National Science Foundation and collaboration with the Smithsonian Institution are gratefully acknowledged.

[1] Meyer E., *IEEE Eighth International Conference on Information Visualisation*, London, 2004, 229-234.

**Keywords:** computer graphics, models, sculptures

### MS31 SUPRAMOLECULAR CHEMISTRY

**Chairpersons:** Franco Ugozzoli, Claire Gervais

#### MS31.26.1

*Acta Cryst.* (2005). A61, C44

#### Diffusion of Guests into Non-porous Crystals

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Crystals composed of purely organic compounds have largely been ignored as gas sorption substrates since such molecules usually pack with efficiencies in the narrow range of 60 to 67%. The host lattices of solvated inclusion compounds are often described as possessing zero-, one-, two- or three-dimensional solvent-accessible voids if the guest molecules are located in isolated cavities, channels, layers or networks of channels, respectively. It is therefore attractive to envision facile removal of the solvent molecules from these materials to yield highly porous host lattices analogous to those of zeolites. In reality, the process of desolvation almost always involves reassembly of the host molecules in the solid state to form one or more phases, where the pure compound is again efficiently packed. However, a few exceptions are known to exist. A low-density phase of sublimed *p*-*tert*-butylcalix[4]arene possesses lattice voids of *ca.* 235 Å<sup>3</sup> [1]. Despite an apparent lack of porosity, these crystals readily and reversibly absorb volatile gases [2,3] at room temperature and ambient pressures. In this presentation, new developments in the understanding of such gas absorption will be discussed.

[1] Atwood J. L., Barbour L. J., Jerga A., Schottel B. L., *Science*, 2002, **298**, 1000. [2] Atwood J. L., Barbour L. J., Jerga A., *Angew. Chem. Int. Ed. Engl.*, 2004, **43**, 2948. [3] Atwood J. L., Barbour L. J., Thallapally P. K., Wirsig T. B., *Chem. Comm.*, 2005, 51.

**Keywords:** calixarene, gas absorption, single crystal

#### MS31.26.2

*Acta Cryst.* (2005). A61, C44

#### Sandwiches and Cavities: The Supramolecular Chemistry of Hemimellitic Acid

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Prior to our investigations of its potential contribution to supramolecular chemistry, and despite its commercial availability as a crystalline dihydrate, hemimellitic acid (H<sub>3</sub>HMA; benzene-1,2,3-tricarboxylic acid) appeared in only 8 crystal structures recorded in the Cambridge Structural Database (CSD; Version 5.26, November 2004).

The presence of carboxylic acid functionality in H<sub>3</sub>HMA facilitates the formation of both organic-based hydrogen bonding arrays and metal-organic coordination frameworks, as has been previously demonstrated using trimesic and terephthalic acids.

H<sub>3</sub>HMA forms solvent-inclusion clathrates with solvent molecules capable of hydrogen bonding, often with rectangular solvent-filled cavities running through the structure [1]. Co-crystallisation with molecules containing *N*-heterocycles has also led to hydrogen bonded structures, often with accompanying proton-transfer [2]. The most interesting findings undoubtedly result from a systematic study of the coordination of H<sub>3</sub>HMA to monopositive (Group 1 metals) and dipositive (Group 2 and transition metals) cations [3]. Significant structural diversity has been observed within this series of complexes; trends within the series will be analysed.

[1] Dale S. H., Elsegood M. R. J., Coombs A. E. L., *CrystEngComm*, 2004, 328-335. [2] Dale S. H., Elsegood M. R. J., Kainth S., *manuscripts in preparation*. [3] Dale S. H., Elsegood M. R. J., Kainth S., *manuscripts in preparation*.

**Keywords:** supramolecular chemistry, hydrogen bonding, carboxylic acids

#### MS31.26.3

*Acta Cryst.* (2005). A61, C44

#### Supramolecular Coordination Chemistry – the Challenge of the Outer Sphere

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Supramolecular coordination chemistry seeks to construct large complexes, either as discrete multinuclear complexes or as extended structures. Synthetic approaches may be classified into: (A) the use of large polynucleating ligands capable of binding several metal ions; (B) the use of bridging ligands such as 4,4'-bipyridine, cyanide or oxalate to link metals together; (C) linking complexes via interactions between groups located on the exterior of the complex, the outer sphere. This last approach is the subject of the lecture. It offers a number of advantages including easier synthesis than approach (A), and little or no perturbation of the properties of the metal centre. In favorable cases the binding of the metal can be used to activate the ligand to outer sphere association, and the interaction may be controlled by the external environment.

These ideas will be illustrated by a series of examples using hydrogen bonding and stacking interactions of heterocyclic ligands. Attention will be paid to how these interactions may be induced or suppressed.

**Keywords:** coordination compounds, supramolecular chemistry, crystal packing

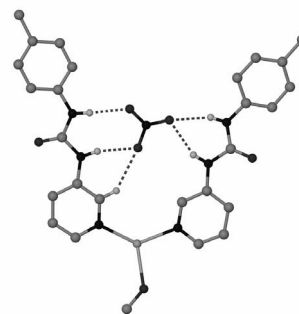
#### MS31.26.4

*Acta Cryst.* (2005). A61, C44-C45

#### Structure Control by Hydrogen Bonding to Anions and Coordination to Cations

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A series of urea-containing pyridyl ligands have been prepared and used to bind ion pairs by hydrogen bonding to the anions and coordination to the cations. The new complexes are frequently coordination polymers or hydrogen bonded polymers, although discrete species that also persist in solution have also been observed (as in the figure). Common, reproducible and predictable hydrogen bonded motifs are observed across the series.



[1] Turner D. R., Spencer E. C., Howard J. A. K., Tocher D. A., Steed J. W., *Chem. Commun.*, 2004, 1352. [2] Turner D. R., Light M. E., Hursthouse M. B., Steed J. W., *Chem. Commun.*, 2004, 1354. [3] Turner D. R., Smith B., Goeta A. E., Evans I. R., Tocher D. A., Howard J. A. K., Steed J. W., *Cryst. Eng. Comm.*, 2004, 6, 633. [4] Turner D. R., Smith B., Spencer E. C., Goeta A. E., Evans I. R., Tocher D. A., Howard J. A. K., Steed J. W., *New. J. Chem.*, 2005, 29, 90.

**Keywords:** anion, hydrogen bond, motif

### MS31.26.5

*Acta Cryst.* (2005). A61, C45

#### Molecular-Level Devices and Machines

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The chemical, bottom up approach, based on the concepts of supramolecular chemistry, can be very useful to design and construct interesting nanostructures.

By using this approach, the macroscopic concepts of a device and a machine can indeed be straightforwardly extended to the molecular level [1]. A *molecular-level* device can be defined as an assembly of a discrete number of molecular components designed to achieve a specific function. Each molecular component performs a single act, while the entire assembly performs a more complex function, which results from the cooperation of the various molecular components. A *molecular-level machine* is a particular type of molecular-level device in which the component parts can display changes in their relative positions as a result of some external stimulus.

Molecular-level devices and machines operate via electronic and/or nuclear rearrangements and, like macroscopic devices and machines, are characterized by (i) the kind of energy input supplied to make them work, (ii) the way in which their operation can be monitored, (iii) the possibility to repeat the operation at will (cyclic process), (iv) the time scale needed to complete a cycle, and (v) the performed function. In this lecture, we will illustrate examples of recent achievements in this field.

[1] Balzani V., Credi A., Venturi M., *Molecular Devices and Machines - A Journey in the Nano World*, Wiley-VCH, 2003.

**Keywords:** supramolecular chemistry, photochemistry, electrochemistry

### MS32 STRUCTURE DETERMINATION FROM POWDER DIFFRACTION DATA (INORGANICS)

**Chairpersons:** Angela Altomare, Holger Putz

#### MS32.26.1

*Acta Cryst.* (2005). A61, C45

#### Exploiting Preferred Orientation to Resolve the Intensities of Overlapping Reflections

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In 1999, Wessels *et al.*[1] demonstrated the practical viability of the 'texture method' for resolving reflections that overlap in a powder diffraction pattern. By collecting synchrotron data on a textured polycrystalline sample as a function of sample orientation, more information about the relative intensities of overlapping reflections could be obtained. A full texture analysis is used to establish how the crystallites are oriented in the sample, and then a single set of (single-crystal-like) reflection intensities is extracted via a joint refinement procedure using all diffraction patterns (between 5 and 1296) simultaneously. The data collection and analysis strategies for both reflection and transmission geometries have been described [2]. To develop the method further so that even more complex structures can be accessed, several possibilities are being explored. (1) A new method for preparing textured powder samples using a repetitive pressing procedure has been developed. (2) To optimize the resolution of the data, diagonal displacement of the imaging plate at

the maximum sample-to-detector distance has been evaluated. (3) To improve the resolution still further, an experimental setup with a one-dimensional Si-microstrip detector, has been devised. (4) A new background and scaling procedure has been implemented in the data analysis software.

[1] Wessels T., Baerlocher Ch., McCusker L.B., *Science*, 1999, 284, 477. [2] Baerlocher Ch., McCusker L.B., Prokic S., Wessels T., *Z. Kristallogr.*, 2004, 219, 803.

**Keywords:** powder diffraction, preferred orientation, structure solution

#### MS32.26.2

*Acta Cryst.* (2005). A61, C45

#### New Strategies for the *ab-initio* Structure Solution in EXPO2005

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The full pathway in the *ab-initio* crystal structure solution from powder data has been made more straightforward by the package EXPO2004 [1] which is able to: index the diffraction pattern; identify the most plausible space group; estimate the reflection integrated intensities; solve the crystal structure by Direct Methods, in eventual combination with Monte Carlo approach; refine the structure model by Rietveld technique.

New strategies have been recently introduced in EXPO2004 in order to enhance its power, leading to EXPO2005. Among them the most relevant are: a) an improved algorithm for space group determination; b) a new definition of the background contribution; c) efficient methods for estimating the integrated intensities via a systematic procedure based on coding theory and/or Patterson inversion technique; d) an effective figure of merit able to identify the most plausible phases set; e) a powerful global optimization approach to be applied in case of organic structures; f) a more robust structure refinement procedure.

The EXPO2005 features and applications will be described.

[1] Altomare A., Caliendo R., Camalli M., Cuocci C., Giacobuzzo C., Moliterni A.G.G., Rizzi R., *J. Appl. Cryst.*, 2004, 37, 1025-1028.

**Keywords:** *ab-initio* structure determination, powder software, computational crystallography

#### MS32.26.3

*Acta Cryst.* (2005). A61, C45-C46

#### Are Well Known Phase Diagrams Really Well Known ?

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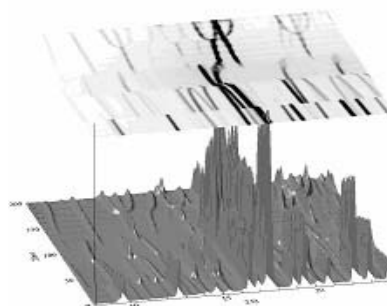


Fig. 1: Temperature dependent powder patterns of  $RbC_2O_4$  [1].

Phase diagrams, which show the preferred physical states of matter at different temperatures and/or pressure, are available for many common substances near ambient conditions. The number of previously unidenti-fied polymorphic phases increases considerably even for "well known" compounds (see Fig. 1) if the technique of high-throughput *in-situ* synchrotron powder diffraction in combination with fast 2D-detectors is applied. The main problem is related to the enormous amount of data which need to be processed efficiently. Techniques to solve part of this problem [2] are presented during the talk.