

FA4-MS03-P01**The Supramolecular Assemblies of a Selection of Imidazole Derivative and Dicarboxylic Acid Salts.**

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Although recrystallisation of a heteromeric solution is commonly used as a method of purification, it may also result in the formation of a salt. Salt formation is a technique often used by the pharmaceutical industry to enhance the physicochemical, formulation, biopharmaceutical, and therapeutic properties of a drug without modifying the basic chemical structure[1]. It would be of great benefit to chemists and formulators to be able to predict the effect various salt formers have on a drug. As the properties of the salt are derived from its crystal structure, we have performed a systematic study of solid forms consisting of simple organic molecules with weakly interacting functional groups in order to gain more understanding of the process of salt formation.

This study involved reacting a large number of simple nitrogen-containing compounds with α,ω -dicarboxylic acids (diacids), including alkane, alkene and hydroxy diacids. The work presented here describes sixteen salts (twelve synthesised and four obtained from the literature[2]) containing imidazole, 1-methylimidazole, 2-methylimidazole, 4-methylimidazole or 1,2-dimethylimidazole. The products were characterised by single crystal X-ray diffraction and the intermolecular interactions between the functional groups in each of the crystal structures were compared. It was found that these sixteen salts all formed similar sheet structures which could be depicted schematically, incorporating the direction of the anion chains, and the orientation of the imidazole methyl group within the sheet. The deprotonation patterns of the diacids, the effect of the methyl group together with its position on the imidazole ring, and the importance of C-H...O hydrogen bonding interactions in the sheet structures are assessed.

[1] P. H. Stahl, C. G. Wermuth (Eds.), *Handbook of Pharmaceutical Salts Properties, Selection and Use*, Wiley-VCH, Zürich, 2002. [2] J.C. MacDonald, P.C. Dorrestein, M.M. Pilley, *Cryst. Growth Des.*, 2001, 1, 29-38.

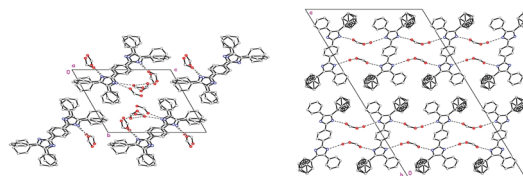
Keywords: salt; supramolecular; hydrogen bonding

FA4-MS03-P02

Supramolecular Associations in Bisimidazole Derivative/formic Acid Solvates. Lidiya Izotova^a, Jamshid Ashurov^a, Samat Talipov^a, Bakhtiyar Ibragimov^a, Edwin Weber^b. ^a*Institute of Bioorganic Chemistry, Tashkent, Uzbekistan.* ^b*Institute für Organische Chemie, TU Bergakademie Freiberg, Germany.*

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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 1:2:2H₂O. 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.

Keywords: crystal engineering; hydrogen bonding; supramolecular assemblies

FA4-MS03-P03**The Crystal Structure, Substructure and Properties of Langatate.**

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Langatate crystals ($\text{La}_3(\text{Ga}_{0.5}\text{Ta}_{0.5})\text{Ga}_5\text{O}_{14}$ – LGT, sp.gr. P321) are the most promising materials for making both bulk acoustic and surface acoustic waves devices. The aim of this paper is to exhibit a role of some growth conditions in a property peculiarities and structural perfection of LGT. Crystals with dimensions 3" have been grown in $\langle 0001 \rangle$

(Z-crystals) and $\langle 01\bar{1}1 \rangle$ (Y54°-crystals) directions by Czochralski technique. They were analyzed by X-ray (CAD-4 and Xcalibur diffractometers, MoK_α) and neutron (TriCS diffractometer, $\lambda=1.18\text{\AA}$; diffractometer located at the channel 5C2, $\lambda=0.83\text{\AA}$) diffraction methods. The refinement of the crystal structure was carried out using

SHELXL97 program. Samples had significantly different colors, depending on the growth atmosphere (Ar+O₂: yellow or orange) and post-grown treatment (Ar and vacuum: almost colorless; air: bright orange). The analysis of the color and crystal composition of La₃(Ga_xTa_{1-x})Ga₅O_y allowed to divide them into four groups: colorless (y~14), orange (y~13.95-13.97), yellow (y~13.92-13.93), and colorless (y~13.90). These results are agreed with transmission spectroscopy («Specord-M40», wave range 11000-50000 cm⁻¹): the yellow crystals with the oxygen vacancies (□) have the band 28500 cm⁻¹. The low-grade band 20800 cm⁻¹ is present at colored crystals and absent at colorless ones (the like result has been wrote in [1]). At that the study of their chromaticity diagrams showed the different shade for the samples of the like visual color. The orange and colorless (the last group) Y54°-crystals, Y54° cut and the orange, yellow and colorless (the first group) Z-crystals, Z cut have the microhardness value ~13.8, ~12.2 GPa and ~12.6, ~10.4 and ~9.7Gpa, respectively. It was found that the temperature maximum of the yellow plate (Z-crystal, Z-cut) dielectric loss tangent has an effusive relaxation maximum in the temperature range 300-550°C. The topography by Shultz method (reflection 50.0) of the yellow plate (Z-crystal, Z-cut) with the refined composition La₃(Ga_{0.58}Ta_{0.42})Ga₅(O_{13.92}□_{0.08}) shown absence of blocks. According to the rocking curves (the scheme of a double-crystal X-ray diffractometer: Si (400) monochromator, (n, -n)) of the same sample, the half-width of the Bragg 50.0 and 40.0 peaks (value β_{exp}) are ~22" in contrast to the Z-crystal LGT, Y cut [2], in which β_{exp} ~6". So, a series of properties of LGT can be associated with the atmosphere of growth and post-grown treatment (the composition of crystals and their color), the growth and cut directions (the microhardness and structural perfection). Moreover langatate crystals are more appropriate for the high temperature applications compared with langasite ones.

[1] O.A.Buzanov et al., Crystallography Reports, 52(4) 2007,691-696. [2] D.V.Roshchupkin et al. Bulletin of the Russian Academy of Science: Physics. 72 (2) 2008, 184-187

Keywords: piezoelectrics; single crystal X-ray diffraction; microstructure characterization

FA4-MS03-P04

Simple Decoration of Inclusion Cavities within Isostructural Two-Component Organic Salts. Judit Galcera^a, Tomislav Friščić^b, Elies Molins^a, William Jones^b. ^aInstitut de Ciència de Materials de Barcelona Campus UAB, 08193 Bellaterra, Spain. ^bDepartment of Chemistry, University of Cambridge Lensfield Road, CB21EW Cambridge, UK. E-mail: jgalcera@icmab.es, wj10@cam.ac.uk

The rational design of multi-component crystalline organic solids is an important developing area in chemistry, especially for its applications in pharmaceutical and material sciences. The synthesis and screening for such multi-component solids (e.g. cocrystals) is significantly facilitated by using liquid-assisted grinding (LAG)¹. In this contribution, we

describe how LAG revealed an unprecedented number of 30 isostructural three-component molecular solids, based on the pharmaceutical compound lamotrigine. The solids are based on a two-component ionic inclusion host, composed of lamotrigine cations and a variable anion, along with an included solvent.² The ability to modify the anion components of the host provides a unique opportunity to manipulate the size and shape of the inclusion cavity, whilst maintaining the isostructurality of the material.

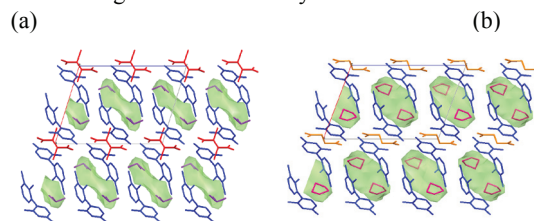


Figure 1. Different shapes of the inclusion cavities in lamotrigine D,L-chlorosuccinate (a) and lamotrigine succinate (b).

Consequently, the materials that will be described in this presentation illustrate a novel methodology to functionalise inclusion cavities and achieve control over molecular inclusion in organic solids, without resorting to rigid structures, such as metal-organic frameworks.

[1] T. Friščić, A.V. Trask, W. Jones and W. D. S. Motherwell *Angew. Chem. Int Ed.* 2006, 45, 7546. [2] J.Galcera and E.Molins *Cryst. Growth Des.* 2009, 9, 327.

Keywords: isostructurality; organic inclusion compounds; supramolecular host-guest chemistry

FA4-MS03-P05

Orientation ordering of the fullerene molecules in the ionic multicomponent complex (MDABCO⁺)(C₆₀⁻)·TPC. Salavat Khasanov^a, Dmitry Konarev^b, Gunzi Saito^c. ^aInstitute of Solid State Physics, Chernogolovka, Russia. ^bInstitute of Problems of Chemical Physics, Chernogolovka, Russia, ^cMeijo University, Nagoya, Japan. E-mail: khasanov@issp.ac.ru

The crystal structure of the ionic multicomponent complex (MDABCO⁺)(C₆₀⁻)·TPC incorporates two crystallographically independent close packed fullerene layers. At room temperature one of them completely ordered while in the other one the molecules are almost freely rotating. There are three stages of fullerene ordering in the disordered layer. Firstly it takes place a dynamical ordering down to 200K, when the fullerene motion can be approximated well by jumping only between three orientations with equal occupancies (33%). Occupational ordering in the temperature range 200-180K lowers the crystal structure symmetry from the trigonal to the monoclinic one. Complete ordering is resulted in the lattice distortion to the triclinic symmetry, which is accompanied by twinning of crystal sample. Full crystal structure analysis has been carried out for the all temperature ranges with