

valine and d-alanine take place below 270K, and they do not appear in 1-equivalents. Recently, the phenomenon was investigated using differential scanning calorimetry and laser Raman spectroscopy [1]. It was also studied by X-ray diffraction (elementary cell against the temperature measurements) [2], and neutron diffraction (structure solution and refinement) [3]. These studies have questioned previous findings.

Because both diffraction methods do not consider subtle electronic effects, we have decided to apply experimental charge density methods to investigate these possible phase transitions. Here in this communication we present a comparison of charge densities of selected amino acids which have been not determined so far.

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Keywords: charge density, amino acids

MS90.P03

Acta Cryst. (2011) **A67**, C761

Multi component crystals of active pharmaceutical ingredients: 1,1-dimethylbiguanide hydrochloride, diflunisal and valproic acid

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The design of multi-component crystals requires knowledge of robust supramolecular synthon. We explore the applicability heterosynthons based on O-H...N and N-H...O hydrogen bonds for the synthesis of pharmaceutical multi-component crystals with three important pharmaceutical molecules: the anti-diabetic drug 1,1-dimethylbiguanide hydrochloride (1), the anticonvulsant drug valproic acid (2), the anti-inflammatory drug diflunisal (3). Both traditional solution co-crystallization and solvent-drop grinding co-crystallization have led to the discovery of 1,1-dimethylbiguanide-oxalate monohydrate salt (1:2.5), methylbenzylammonium-valproate salt (1:1) and diflunisal-hexamethylenetetramine (1:1) co-crystals. In the course of the experiments a new hydrate of succinic acid was obtained.

Keywords: co-crystallization, multi-component crystal, hydrogen bonding.

MS90.P04

Acta Cryst. (2011) **A67**, C761

Experimental charge density distribution in *N*-o-vanillylidene-L-histidine

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Charge density distribution in the crystal structure of *N*-o-vanillylidene-L-histidine (OVHIS) has been determined by using of a high-resolution, low-temperature, single-crystal X-ray diffraction data set. The Hansen-Coppens multipole model [1] was used to describe the electron density distribution in the OVHIS molecule. It was found that OVHIS exists in a double zwitterionic form. Four oxygen atoms in the molecule are approximately coplanar, carry significant negative charge and they together form an area of strong negative electrostatic potential. The OVHIS molecule is very polarized and has a high molecular dipole moment in solid state. A topological analysis of the total electron density, based on Bader's Quantum Theory of Atoms in Molecules (QTAIM) [2], confirmed the existence of 12 intermolecular interactions and corresponding (3,-1) bond critical points. It seems that intermolecular hydrogen bonds (especially two strong charge-assisted N-H...O bonds) significantly contribute to existing charge density distribution in the OVHIS molecule and its electrostatic properties.

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Keywords: zwitterion, charge density distribution, electrostatic properties

MS90.P05

Acta Cryst. (2011) **A67**, C761-C762

Rerefinement of tricyclic acyclovir: C₁₁H₁₃N₅O₃·2H₂O

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Tricyclic acyclovir, 3-[(2-hydroxyethoxy)-methyl]-6-methyl-3*H*-imidazo[1,2-*a*]purin-9(5*H*)-one, has been reported as the dihydrate, C₁₁H₁₃N₅O₃·2H₂O. The complex concerted hydrogen bond network of water and tricyclic acyclovir molecules was suggested to be related to the solvation of the molecules in solution [1]. The *Z'* = 2 structure contains four independent solvent water molecules, forming an (H₂O)₈ cluster through a strong hydrogen bond (d[O...O] = 2.81 Å) between two water molecules across an inversion center. Three of the independent water molecules are ordered while the inversion center requires one hydrogen atom in the fourth to be statistically disordered. The second disordered hydrogen position is a strong donor to the hydroxyl group of the side chain of one independent molecule of tricyclic acyclovir. The hydroxyl group in turn relates to an equivalent group on the next molecule through a strong hydrogen bond (d[O...O] = 2.67 Å) across another inversion center requiring statistical disordering of the hydroxyl hydrogen atom [2]. The result of the hydrogen atom disorders is concerted chains propagating in opposite directions, which differ only in the placement of the hydrogen atoms.

The (H₂O)₈ clusters are essentially perpendicular to the chains and create a 2D network with both independent tricyclic acyclovir molecules, using strong O-H...O water-water and water-drug, and O-H...N water-drug interactions linking the entire structure into an extensive, strong 3D hydrogen bonded network. The supramolecular interactions of the disordered side chain disorder of tricyclic acyclovir provide a rationalization of the nonstatistical disorder previously reported [1] through clear C-H...O preferences for the major component at two atom sites, no clear preference at the ether oxygen atom site, and a weak C-H...O preference at one minor component site.

Poster Sessions

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Keywords: disorder, supramolecular structure, acyclovir

MS90.P06

Acta Cryst. (2011) **A67**, C762

Crystal structure of two new carbacylamidophosphates

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In recent years, carbacylamidophosphates with the C(O)NHP(O) skeleton have attracted much attention due to their properties as prodrugs [1,2], ureas inhibitors [3], and efficient ligands in coordination chemistry either as O-donor or O,O'-donor ligand [4,5]. In earlier works we considered the structural properties of some of these molecules with formula C₆H₅CONHPO(R')₂. To further investigate this area, here we have synthesized two new compounds with general formula C₆H₁₁C(O)NHP(O)R₂, R= 2-ClC₆H₄CH₂NH (**1**) and C₆H₁₁NH (**2**) and present their X-ray crystal structures.

Colorless crystals of **1** and **2** were obtained from a concentrated chloroform solution at room temperature. The compounds **1** and **2** crystallize in the triclinic and Orthorhombic systems with space groups *P*-1 and *Pmn*2₁ respectively. In the structure of compounds **1** and **2**, as in the most carbacylamidophosphates [6], the carbonyl and phosphoryl groups are in anti-positions to each other, and the bond lengths (1.226(2) and 1.4797(13) in **1**; 1.219(5) and 1.478(3) Å in **2** respectively) fall within the norms for these linkages. The dihedral angles between the PO double bond and the N-C amidic bond are -166.04(15) and 180° in **1** and **2** respectively. The phosphorus atoms have a slightly distorted tetrahedral configuration with angles in the range of 101.18(10)–119.75(8)° in **1** and 102.50(16)–116.25(10)° in **2**. As expected, the P–N_{amide} bond length (N_{amide}: the nitrogen atom of P(O)N(H)C(O) moiety) is longer than the P–N_{amine} distances (N_{amine}: the nitrogen atom of P(O)NHR moiety) and the C–N_{amide} bond is shorter than the C–N_{amine} bond lengths (1.374(2) Å for C–N_{amide} versus 1.453(2) and 1.469(2) Å for C–N_{amine} bonds in **1**). All of the P–N bonds in **1** and **2** are shorter than the typical P–N single bond length (1.77 Å) [7]. This is likely due to the electrostatic effects which overlap with P–N σ bond.

The two molecules in the unit cell of **1** are coupled into centrosymmetric dimers by two H-bonds between the phosphoryl oxygen atoms and the hydrogen atoms of the amidic groups forming an eight-membered cycle. The observed hydrogen-bonding pattern is of the DA = AD type. The dimers are linked into 1D chains along the *a* axis by means of another centrosymmetric hydrogen bonds of the DA = AD type involving the oxygen atoms of carbonyl groups and hydrogen atoms of 2-chlorobenzylamine groups (N2–H2 and N3–H3).

The O(1) oxygen atom in **2** functions as bifurcated acceptor and is involved in intermolecular hydrogen bonds with NH groups of cyclohexylamines. As a result of this type of hydrogen bonding and N(1)–H(1N)...O(2) interactions, 1D chains along the *b* axis are obtained.

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Keywords: crystal structure, carbacylamidophosphate, hydrogen bond

MS91.P01

Acta Cryst. (2011) **A67**, C762

X-ray fluorescence imaging of ancient artifacts

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Synchrotron-based X-ray fluorescence imaging (XRFI) is a powerful tool for examining archeological artifacts. Many artifacts have been damaged by weathering and other processes, often to the point where letters or figures have become difficult or impossible to see by visual or topographic inspection. XRFI allows imaging of elemental concentrations, and can detect minute remaining traces of elements arising from paints, pigments and tool wear associated with the original pattern. Since X-rays penetrate a significant distance beneath the surface, XRFI can see through overlayers of paint and debris and can detect elements that have soaked or diffused into stone substrates.

We have imaged a large number of ancient Greek and Roman inscriptions on stone [1] and a variety of Mayan artifacts. Element maps have revealed significant new information, including letters outlined by traces of iron from tools and lead from pigments, and painted designs which were previously invisible due to overpainted layers. They have also proved useful in establishing inscription provenance [2]. Opportunities and challenges in applying XRFI to ancient artifacts will be discussed.

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Keywords: X-ray fluorescence imaging, epigraphy, archaeology

MS91.P02

Acta Cryst. (2011) **A67**, C762–C763

Opacity in mosaic glass: crystals make technological history

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Opaque glass represents the first record of glass production at the end of the second millennium AD in Mesopotamian region. The opacity of glass, in most of the cases, is given by the presence of crystalline phases dispersed in the glass matrix. The crystal phases used as opacifiers changed across the centuries and different compounds were used to obtain the opaque effect and the desired nuances. Antimony-based opacifiers (lead antimonate yellow and calcium antimonate white)