MS19 P01

Molecular assembiles of protein degradation pathways in prokaryotes and eukaryotes Borissenko L, Groll M. Department of Structural research, Institute of Biochemistry, Charité Medical School of Humbold University of Berlin, Monbijoustrasse 2, 10117 Berlin, Germany

Keyword 1 : proteolysis, crystal structure, proteasome

Protein degradation is an essential and strictly controlled process with proteasome and functionally related proteases representing its central part. Tricorn protease (TRI) has been shown to act downstream of the proteasome, degrading produced peptides. Recently, a novel large prokaryotic aminopeptidase oligomeric complex, named TET, has been identified. This complex degrades peptides of different length in organisms where TRI is not present. We determined the crystal structure of TET from the thermophilic archaeon Pyrococcus horikoshii at 1.6 A resolution in native form and in complex with the inhibitor amastatin. We demonstrate that, beside the novel tetrahedral oligomerisation pattern, TET possesses a unique mechanism of substrate attraction and orientation. TET sequentially degrades peptides produced by the proteasome to single amino acids. Furthermore, we reconstituted in vitro the minimal protein degradation system from initial unfolding of labelled protein substrates, up to release of free amino acids. We propose that TET and TRI act as functional analogues in different organisms, with TET being more widely distributed. Thus, TET and TRI represent two evolutionarily diverged pathways of peptide degradation in prokaryotes. Our current interest is to follow the mechanisms of supramolecular assemblies which occur during the process of proteolysis in pro- and eukaryotes, using combination of various structural, biochemical and biophysical methods. Participants of the proteolytic process such as unfoldases, proteasome and downstream peptidases are marked with fluorescent tag-proteins or dyes in order to visually follow the formation of complexes upon addition of the substrate protein/peptide.

MS19 P02

Synthesis, Structure and Non-Linear Optical Activity of New 1D, 2D, and 3D Cadmium(II) and Zinc(II) Azido complexes. Morsy M.A.M. Abu-Youssef[a], Vratislav Langer[b], Alshima'a A. Massoud[b], Maher Abd El-Megeed Farhoud[c], *[a]Chemistry Department, Faculty of Science, Alexandria University, Egypt. [b]Environmental Inorganic Chemistry, Department of Chemical and Biological Engineering, Chalmers University of Technology, Sweden. [c]Physics Department, Faculty of Science, Alexandria University, Egypt.*
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Keywords: complexes, azides, NLO

The design and synthesis of versatile molecular building blocks towards self-assembly functional materials is one of our interests. New thermally stable coordination compounds based on 3D nets were synthesized and characterized. Cadmium (II) and zinc (II) azido polynuclear complexes were found to have not only an intriguing structures but also Non-Linear Optical (NLO) properties. Recently we have synthesized a series of high dimensionality Cd (II) and Zn (II) azido complexes: **3D**-$[Cd_3(nic)_4(N_3)_2(H_2O)_2]_n$ **(1)**, $[Zn(nic)(N_3)]_n$ **(2)**, and $[Cd(2,5\text{-dmpyz})(N_3)_2]_n$ **(3)** , **2D**- $[Cd(Quz)_2(N_3)_2]_n$ **(4)**, **1D**-$[Zn(bipy)(N_3)_2]_n$ **(5)**, $[Cd(bipy)(N_3)_2]_n$ **(6)**, $[Cd(Qux)_2(H_2O)]_n$ **(7)** and $[Cd(2\text{-acpy})(N_3)_2]_n$ **(8)**, where (nic = nicotinate anion; 2,5-dmpyz = 2,5-dimethylpyrazine, Quz = quinazoline, bipy = 2,2'-bipyridyl, Qux = quinoline-4- carboxylato anion and 2-acyp = 2-acetylpyridine), [1-4]. Most of these complexes show higher second harmonic generation (SHG) efficiency than $LiNbO_3$ and potassium dihydrogen phosphate (KDP). Coordination polyhedra of $[Cd_3(nic)_4(N_3)_2(H_2O)_2]_n$, **(1)**

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MS19 P03

Redetermination of the A-amylose crystal structure
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Keywords: amylose, single-crystal X-ray diffraction

The structure of A-amylose has been revisited by single-crystal microdiffraction. This allows determining of structural differences as compared to previous fiber and powder diffraction data [1]. Recent progress in synchrotron radiation microdiffraction [2] has now made feasible the collection of X-ray data sets on micrometer sized single crystals. In the present note we report the crystal structure of A-amylose based on low temperature synchrotron radiation microdiffraction. Needle-shaped A-amylose single crystals of less than 15 □m length and about 2 □m thickness have been crystallized from diluted aqueous solutions of amylose fractions [3]. Experiments were performed at the ESRF ID13 beamline at wavelength of λ=0.9465 Å. The beam was focused by parabolic Be-refractive lenses and collimated to either 10μm or 30μm at the ID13 microgoniometer [2]. Diffraction patterns were recorded at 100K by a MAR165 CCD and processed by XDS data reduction package [4]. We have already reported previously unit cell parameters and space group (B2) of A-amylose [5]. The intensity data collected on 14 crystals were merged together using XSCALE software [4]. The resulting data set has 1.3Å highest resolution, average I/σ 9.37 and redundancy 5.9. The structure of A-amylose was solved by molecule replacement technique using PATSEE software [6]. A fragment of a regular 6-fold helix of 3 residues length was used as a search fragment. Positions of primary hydroxyl groups and all positions of water molecules were found on electron difference map. The structure was refined in isotropic approach of thermal parameters using restraints up to R1=0.1749, R_{free}=0.2216. The principal structural model obtained is the same as determined previously by X-ray powder and fiber methods [1]. The basic units of the A-amylose crystal framework are six-fold left-handed double helices having *gauche-gauche* conformations of primary hydroxyl groups. The helices are arranged around two fold symmetry axes and have repeat 2*c*=2.116 nm. The present

study has also revealed some flaws in the previous model of inter-double-helix hydrogen bonding.

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MS19 P04

Fullerene – Fullerene Interactions in the Crystals of the Fullerene C_{60} Organic Derivatives

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Keywords: fullerenes, crystal packing, amphiphilic properties

Functionally substituted fullerene derivatives are of interest since it is possible to obtain both biologically active substances and new materials for nanotechnology on their basis. The spherical platform of fullerene allows one to design molecules with various fragments, which are responsible for the specific properties. At the same time the crystal structure of such compounds is studied insufficiently, that is why Crystallographic Data Bases contain information about not more than 80 fullerene C60 derivatives structures. Interesting feature of these compounds (both derivatives and fullerene complexes) in solid state is their active participation in pi-electronic interactions between each other and with other compounds incorporating aromatic fragments. Owing to these interactions the compounds can form in a crystal the supramolecular structures of various type, that, apparently, finds reflection in their particular properties.
Basing on literature structural data for organic derivative of fullerene and on our original X-ray data for the bis- and mono-adducts of the methanofullerenes and pyrrolidino-fullerenes, we have analysed the intermolecular interactions, crystal packing and supramolecular structure of these compounds from the point of view of such interactions. It was found, that in spite of the presence of large substituents in the molecules and solvate molecules in the crystals, which hinder such interactions, the fullerene fragments are closely packed with different fullerene environments - honeycomb structure, zigzag-chain, dimers, columns and layers, and preferably interact face-to-face with the 5- and 6-membered aromatic rings. The majority of the compounds forms 2D-structures - layers of various topology with fullerenes coordination equal to 3 or 4. Presence of molecules-guests with aromatic fragments or aromatic fragments in the fullerene derivatives leads to their obligatory participation in such interactions and to the destruction of the fullerene-fullerene interactions.
Recently we carried out the synthesis of malonate nitroxide metanofullerene, which shows, in combination with known anticancer drug cyclophosphamide, the high antitumor activity against leukemia P-388. It was shown by X-ray single crystal analysis that methanofullerene with two nitroxide groups has a diamond-like environment in the crystal due to fullerene-fullerene interactions [1]. In the same time the first examples of the phosphorylated mono- and bis-methano-fullerenes with large substituents have lower coordination of fragments - zigzag chains and pi-dimers. The comparative analysis of the results for the organic derivatives and for the fullerene C60 inclusion compounds is presented. The topology of the crystals is analysed additionally on the base of proposed model of localization of hydrophilic and hydrophobic regions in the crystals of organic compounds.
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MS19 P05

Molecular and Supramolecular Features of Glyoxylamides

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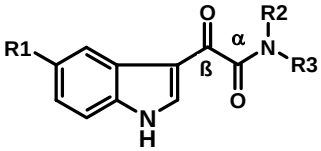
Keywords: hydrogen bonds in organic crystals, conjugated organic compounds, conformational flexibility

Indole-3-ylglyoxylamides are important intermediates in legal and illegal syntheses of pharmaceutically active tryptamine derivatives. We report 3 secondary glyoxylamide structures: I (R1 = R2 = H, R3 = i-Pr), II (R1 = R2 = H, R3 = t-Bu), III (R1 = OMe, R2 = H, R3 = t-Bu).



Secondary glyoxylamides in the Cambridge Structural Database (CSD) always adopt the *syn* conformation with H in the R2 position and O=C-C=O torsion angles within 40° of 180°. Tertiary glyoxylamides have O=C-C=O torsion angles within 40° of 90° or 270°, sacrificing conjugation but alleviating interference between R2 and O. When R2 ≠ R3, the usual *anti* conformation puts the bulkier substituent at R2.