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Double-stranded DNA viruses infect Archae living in hot springs at temperature above 80 °C . They are radically different in their properties from viruses that infect Bacteria and Eukarya. Not only are the shapes of these viruses different to all other viruses found on Earth, but ca 90% of their putative genes do not have any homologs in other viruses or cellular life forms (1). Their ecological, morphological and genomic originality raises intriguing questions about their biology and their origins. Combination of electron microscopy and X-ray crystallography has revealed a nucleosome-like organization for the lipothrixvirus Acidianus Filamentous Virus 1 (AFV1) that has not been yet observed for any linear viruses. The three-dimensional reconstruction of AFV1 core has revealed a left-handed helical structure similar to those in the eukaryal nucleosome. In this architecture, one of the two major structural proteins, the basic ORF132 might form a histone-like central proteic core with the DNA super helix wrapped around. The second structural protein, ORF140, is located peripherally. We propose that its helical and elongated N-terminus, charged positively, is in contact with DNA, probably binding major grooves. The globular C-terminus domain contains an amphiphilic helix and harbours buried octyl-glucoside molecules. It might, together with associated lipids, form the outer coat of the virus. Structural characterizations of these fascinating DNA archaeal viruses, already described with the virus STIV (2), contribute to a recent upsurge of interest in the evolution of virus in general.

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Keywords: virus structure, X-ray macromolecular crystallography, electron microscopy

### MS.36.5

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#### Structural studies of Holliday junction resolvases from bacteriophages, archaea and yeast

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Holliday junctions (HJ) are central intermediates in repair and reorganization of DNA by homologous recombination. HJ-resolving enzymes (also known as HJ resolvases) mediate the resolution of the 4-way junction by introducing symmetrical nicks in opposing strands. Members of this ubiquitous family of structure-specific endonucleases function as dimers and require divalent cations for cleavage. We have previously reported the crystal structure of a HJ complex of Phage T4 endonuclease VII (EndoVII), an enzyme, which is involved in mismatch repair and the resolution of branch points prior to packaging of DNA into the phage head. The conformation of the EndoVII-bound HJ represents a hybrid between the standard stacked-X and square-planar conformations, demonstrating how the junction is recognized and distorted by an induced-fit mechanism. We have also solved the crystal structures of cruciform cutting enzyme

1 (Cce1) from *Candida glabrata* and of the HJ cutting enzyme (Hjc) from the hyperthermophile archaeon *Archaeoglobus fulgidus* at 3 and 1.7 Å resolution, respectively. They represent two structurally distinct resolvase families with the same biological function, but exhibiting clearly different substrate specificities. Recently we have determined the structure of a HJ complex of *A.fulgidus* Hjc at 3.2 Å resolution. Surprisingly, in this complex two Hjc dimers are bound to the junction, which exhibits an essentially undisturbed stacked-X conformation. Common features as well as striking differences in the mode of junction binding and recognition among the structurally characterized members of the resolvase family will be discussed. Biertuempfel, C., Yang, W. & Suck, D. *Nature*, 2007, 449, 616-620.

Keywords: Holliday junction resolvases, endonuclease VII, Hjc, Cce1, crystal structure

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#### Charge density based ligand design

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Recently we synthesised and experimentally determined the charge density in molecular species to gain insight in their reactivity and coordination behaviour. Not to judge on the structure-reactivity relationship by mere bond lengths comparison we rather rely on the topological analysis on the basis of high resolution data and a multipole refinement. Various topics are addressed in the talk:

S=N bonds in polyimidosulfite ylides are rather easy to cleave because they are electrostatically reinforced S<sup>+</sup>—N<sup>—</sup> single bonds rather than hetero-olefin bonds and the formal S=C double bond is a polar S<sup>+</sup>—C<sup>—</sup> single bond with no ylenic contribution;

The same is valid for P=N bonds. Reducing of iminophosphoranes to phosphanes is feasible under the right conditions, even though they are known to be thermodynamic sinks;

The metallaphosphane [Me<sub>2</sub>Al(μ-Py)<sub>2</sub>P] contains a divalent P(III) atom with two lone pairs at the central phosphorus atom. Following this finding the P-atom in the protonated phosphanide PPy<sub>2</sub>(H) can be employed in μ-bridging mimicking a 4-electron donor;

Multipole refinement of an alpha-lithiated benzyl silane provides insight in the electronic situation and thus the observed stereochemical course of transformations. Surprisingly the negative charge generated at the carbanion hardly couples into the phenyl ring;

The Laplacian distribution around the boron atom in [{Cp(CO)<sub>2</sub>Mn}<sub>2</sub>(μ-BtBu)] with its three VSCCs clearly shows the difference between the borylene ligand and the carbonyl ligand. The complex has to be classified as a dimetalloborane with no Mn-Mn bond rather than a borylene complex.

Keywords: ligand design, charge density studies, structure and function

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#### Non-linear optical properties & structure determination by combining X-ray data and QM wavefunctions

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An X-ray constrained wavefunction (XCW) is a wavefunction constrained to reproduce the structure factors from X-ray charge density experiment [1]. XCW's have primarily been used to obtain accurate images of the electron density in molecular crystals [1]. In this talk the XCW method is extended to the calculation of linear and non-linear optical response properties for several molecular crystals [2]. The theory used for the calculation of bulk (crystalline) susceptibilities and refractive indices from molecular polarisabilities will be reviewed. Results for several systems will be presented and discussed. I will also outline a method for improved structure determination based on using aspherical atomic densities obtained from quantum mechanical calculations. The new method allows the determination of ADP's for hydrogen atoms from the X-ray data alone [3]. The possibility of using such aspherical densities in everyday structure refinement will be discussed.

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Keywords: constrained wavefunction, charge density, linear and non-linear optics

## MS.37.3

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### Characterization of weak chemical bonds in highly strained and hypervalent compounds

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To characterize chemical bonds in highly strained and hypervalent compounds have been attractive target of theoretical study. However, it is not rare that some researcher derive different result from other researchers, who study the same compound, especially for such weak chemical bonds. While, if such compounds are synthesized and crystallized, we can perform charge density analysis using accurate X-ray diffraction data, which shows electron density distribution as it is. We report here bonding characters of strained cyclopentyne and 5- and 6-coordinate carbon compounds. Small cyclic alkynes are, in general, unstable because of ring strain. Recently, 1-zirconacyclopent-3-yne complexes, viz 5-membered cyclic alkynes, were synthesized and crystallized.[1] The experimental electron density analysis clarifies that both of the eta2-pi,pi and eta4-pi,pi structures contribute to the bonding not only the former structure.[2] In the case of the 5- and 6-coordinate carbon compounds, we showed dative character of the hypervalent bonds.[3, 4]

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Keywords: charge density, weak chemical bond, synchrotron radiation

## MS.37.4

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### How and why elemental boron undergoes self charge transfer between 19 and 89 GPa

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Boron has nearly 20 polymorphs with non-trivial chemical bonding, complex structures and similar energies. It is the only light element for which the ground state is not experimentally established at ambient conditions. Using high-pressure experiments and an *ab-initio evolutionary methodology*, the structural stability of boron under pressure was explored.<sup>1</sup> At low pressures (<19 GPa) boron adopts covalent structures based on icosahedral B<sub>12</sub> clusters, and at high pressures (>89 GPa) it forms a superconducting  $\alpha$ -Ga-type phase. At intermediate pressures a *new insulating phase*,  $\gamma$ -B, has been found to be stable.<sup>1</sup> Its structure consists of distorted B<sub>12</sub> clusters and B<sub>2</sub> pairs: (B<sub>2</sub>)<sup>Δ+</sup>(B<sub>12</sub>)<sup>Δ-</sup>, with a significant charge transfer (CT), substantiated by several theoretical measures and physical properties. Using Bader's theory,  $\delta$  amounts to  $\approx 0.34$ - $0.48$ , based on either PAW or DFT-LCAO densities. Electron charge flows from B<sub>2</sub> to B<sub>12</sub> units for their corresponding frozen 3D sublattices act as *n*-doped and *p*-doped semiconductors, respectively. The CT occurring in this unique phase affects its physical properties (electronic band gap, infrared absorption, dielectric properties, etc.) and results from the Lewis acid-base interaction of the B<sub>12</sub> and B<sub>2</sub> groups. It is the ability of boron to form clusters with very different electronic properties and the very low packing efficiency of icosahedral structures (34% for  $\alpha$ -B<sub>12</sub>) which leads to  $\gamma$ -B, the *first experimentally established autoionized form of an element*. An analysis of bonding within and between the B<sub>2</sub> and B<sub>12</sub> subunits and its relationship with the observed CT in  $\gamma$ -B is also outlined.

<sup>1</sup>A.R. Oganov, J. Chen, C. Gatti, Y.-Z Ma, *et al.*, Nature submitted

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### Advances in quantum *ab initio* calculations with the CRYSTAL code

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