3.5 Electron Microscopy and Chemical Crystallography (C. W. Lehmann)

Introduction: The EmRay-Group combines all electron microscopy activities of the Institute and selected areas of crystallography, namely crystal structure determination from single crystals and polycrystalline organic materials. The present research fields encompass electron density studies and crystal engineering. In addition to operating in-house facilities the group is part of a team building a dedicated chemical crystallography beamline at PETRA III in Hamburg.

Service Activities, *i) Crystallography:* The service activities focus on single crystal structure analysis and offer powder diffraction of organic compounds as an alternative method for crystal structure determination. The areas general powder diffraction and photon electron spectroscopy have been incorporated in the new research group of Dr. Claudia Weidenthaler.

For single crystal structure analysis state-of-the-art technology is employed, comprising three area detector systems. A Cu-rotating anode equipped with a four circle goniometer and a large surface area CCD-detector is used for the determination of the absolute configuration of enantiopure light atom compounds as well as for protein crystallography. Inorganic and organometallic compounds are investigated using either a Mo-rotating anode or the recently acquired molybdenum micro focus X-ray source, both equipped with four circle goniometers. All diffractometer systems employ graded multilayer optics to maximise X-ray intensities and are equipped with liquid nitrogen low temperature devices for sample cooling and stabilisation. A total of approximately 500 data sets are collected annually, however an increasing number of samples yield only very small crystals with dimensions less than 20 µm. Selected samples are analysed using synchrotron radiation, in particular using the single crystal beamline at ANKA Karlsruhe.

The crystal structures of compounds yielding crystals too small even for synchrotron radiation might be elucidated by means of X-ray powder diffraction. A pre-requisite for the determination of the crystal structures of organic molecules is the knowledge of the atom connectivity. Questions regarding the conformation of the molecules in the solid state as well as to the crystal packing can be answered by this approach. Presently the group has one powder diffractometer for analysing samples enclosed in capillaries or in transmission geometry.

ii) Electron Microscopy: The instrumentation for electron microscopy has remained unchanged during the reporting period. However, an intensive survey followed by demonstrations has been undertaken to identify a suitable microscope for sub-nanometer EDX analysis. This new electron microscope has been ordered and is currently being manufactured. Delivery is expected in the summer of 2014. Presently available electron microscopes in the group comprise a 200 kV TEM with cold field emitter gun, able to obtain micrographs with atomic resolution. Two further 120 kV TEMs supplement the set-up. One of these 120 kV transmission electron microscopes has been dedicated for self-service by trained PhD students and Post-Docs. Scanning electron microscopy is performed with an ultra-high resolution microscope, which gives a line resolution better than 0.34 nm (graphite lattice spacing). An important aspect of the electron microscopy service is the sample preparation, which forms a crucial part of the activities in the group. In addition to established coating and cutting methods, in particular ultra-microtomes, the group is constantly honing its methods and is introducing new techniques as required. Two Master Theses focussed on these aspects over the last years.

Research Projects, *Electron Density Studies (T. Dols):* The DFG priority program 1178 entitled "Experimental Charge Density as the Key to Understand Chemical Interactions" was continued. In collaboration with U. Englert (Aachen) the electron density distribution in metal organic coordination polymers new insight into non-bonding halogen-halogen and halogen-carbon interactions was gained.

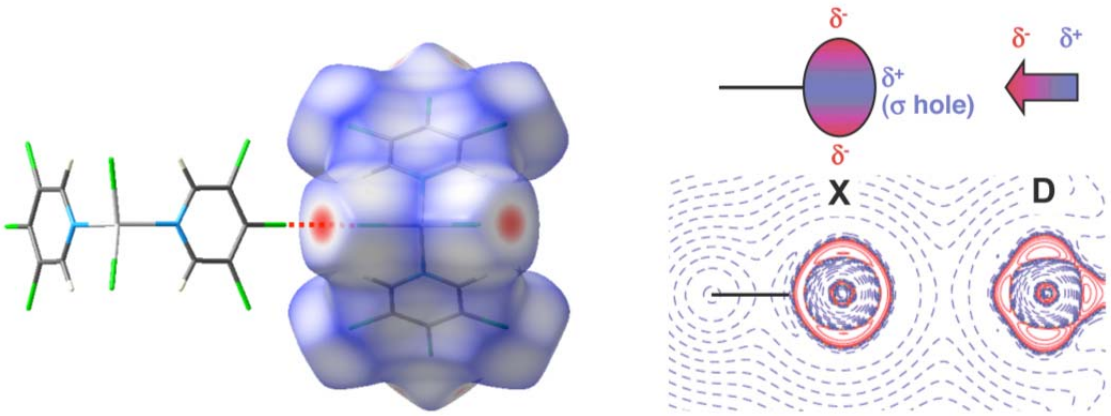
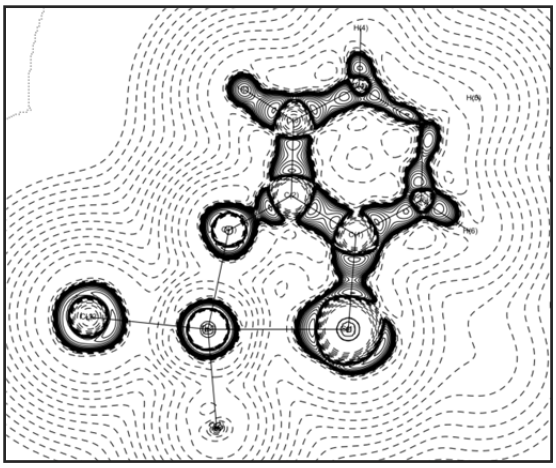


Figure 1: Hirshfeld surface of bis(3,4,5-trichloropyridinyl)zincdichloride (left) showing the short Cl…Cl interaction. Polar flattening of the acceptor halogen is clearly visible in the Laplacian of the electron density (right).

In particular the polar flattening effect postulated for covalently bonded halogen could be observed experimentally.[1] Chemically closely related monomeric zinc-halogen-dipyridyl complexes have been included lately.

Together with T. Spaniol (Aachen) the project on electron density studies of Ti-based stereotactic polymerisation catalysts of the mismatched interaction type was completed.



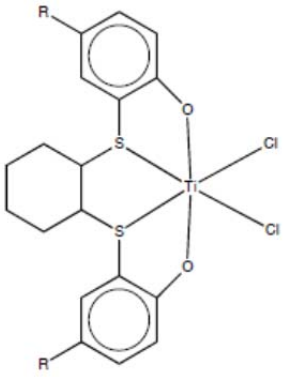


Figure 2: Laplacian of the electron density in the plane subtended by sulfur, titanium and oxygen (left) of the mismatched interaction catalyst shown on the right.

Crystal Engineering (D. Bock): Co-crystals are a specific implementation of supra-molecular chemistry, maximising the use of intermolecular interactions. Liquid assisted ball milling was used to obtain co-crystals composed of chiral carboxylic acids and chiral amides. Combining enantiopure educts in separate experiments it was possible to obtain diastereomeric co-crystals for a number of acid-amide pairs. From clearly distinguishable powder diffraction patterns of the diastereomers it was possible to elucidate not only the crystal structures but also to determine the absolute configuration of one of the two co-crystallised compounds.[2]

Chemical Crystallography Synchrotron Beamline: The extension to the PETRA III synchrotron laboratory at DESY in Hamburg is under construction. Hall East will accommodate the dedicated chemical crystallography beamline P24. A consortium involving the University of Bayreuth (S. van Smaalen), the University of Hamburg (U. Bismayer), the University of Dresden (D. Meyer), the University of Munich (W. Schmahl), and this group has secured BMBF funding for a second period of three years and is responsible for planning, building and commissioning the end-station of this beamline. Specific emphasis is being placed on handling reactive and sensitive samples in a state-of-the-art diffraction set-up. A proof-of-principle experiment has been carried out already at the macromolecular beamline P11. The ChemCryst-beamline, scheduled

for 2015, will permit high resolution single crystal data collections at variable energies up to 40 keV.

Core-shell nano particles (J. von der Heyden): Unambiguous characterization of core-shell particles remains a challenge as the overall diameter of these particles is reduced to about 5 nm. Using synthetic methods developed in the department of heterogeneous catalysis (F. Schüth) core-shell nano particles were synthesized ranging from 5 to 50 nm. At the smaller end of this range a positive identification of the core-shell structure was possible only by using a probe corrected scanning transmission electron microscope equipped with an EDX detector of approx. 1 sr solid angle.

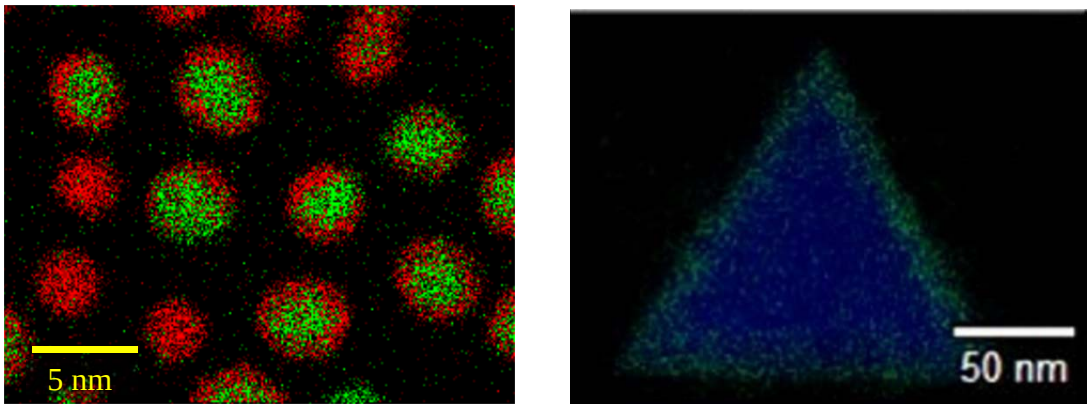


Figure 3: EDX mappings of ruthenium-platinum (core-shell) nanoparticles (left) measured within 10 min. using a C_s corrected STEM and of a Pt@Pd nano-triangle collected using the ultra-high resolution SEM.

Synthetic opals (A.-C. Swertz): A further research project in electron microscopy was directed at preparing cross-sections of synthetic opals (research group of F. Marlow) in order to study lattice defects in these photonic crystals. Using a combination of diamond wire cutting and argon ion milling, cross sections of the as-grown opal films could be obtained for the first time. These were investigated extensively by scanning electron microscopy and revealed unexpected long range domains within the bulk, tilted with respect to the observed {1 1 1} layer formation on the surface.

Publications resulting from this research area:

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Cooperation: U. Englert (Aachen), W. Grünert (Bochum), F. Mohr (Wuppertal), O. Reiser (Regensburg), J. J. Schneider (Darmstadt), T. Spaniol (Aachen), J. Sun (Stockholm), O. Terasaki (Stockholm), H. Willner (Wuppertal)