MS18- Crystallography at high pressure and dynamically compressed matter

Chairs: Dr. Damian Paliwoda, Dr. Ines Collings

MS18-P01

High-pressure single-crystal X-ray diffraction study of a model Rh complex exhibiting metallophilic interactions in the solid state

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High-pressure studies of materials constitute an important field of research, as high-pressure phases often exhibit unique properties, as well as, via applying high pressure one may see what happens to a given material in real-life conditions. The detailed knowledge of materials' structure is indispensable to understand, and later to potentially sensibly control, their behaviour and function. In this respect high-pressure single-crystal X-ray diffraction experiments provide full picture of material's structure with atomic resolution.

Consequently, in this contribution we describe our recent studies of a model rhodium complex, namely $LRh(CO)_2$ (L = 3-benzoylacecate), which exhibits chain substructures based on the Rh…Rh interactions propagating along the Y-axis direction. It is shown the temperature does not have a significant impact on the structural parameters (except for the less obvious unit cell choice in the case of the high temperature structure). In turn, the application of high pressure leads to an interesting phase transition, in which the Rh…Rh chains differentiate noticeably. As a result the structure becomes modulated and has to be treated within a super-space approach. Thus, here the structural analysis of the new modulated phase is presented and the further prospects of using this information to explain spectroscopic behaviour under high pressure are discussed.

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Keywords: High pressure, synchrotron, rhodium complexes, modulated structures, metallophilic interactions

MS18-P02

Structural changes induced by high pressure and radiation in crystals of three cinnamic acid derivatives

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The [2+2] photodimerization was conducted in crystals of 2,5-difluorocinnamic (**1**), 3,5-difluorocinnamic (**2**) and 2,6-difluorocinnamic (**3**) acids in ambient and high-pressure conditions. The photochemical reaction was induced stepwise by UV/vis radiation and the X-ray diffraction experiment was carried out after each step. This enabled us to monitor changes in the unit cell parameters, intermolecular geometry and product content in crystals. The influence of pressure on the direction and size of those changes was analyzed [1].

For each compound there is a critical point below which the increasing pressure speeds up the reaction, and above which the reaction cannot be further accelerated. This is due to the changes in the geometrical parameters describing a pair of reacting molecules and the simultaneous decrease in the volume of free space.

The photochemical reactivity of three studied compounds changed in the following order: (**1**) > (**2**) > (**3**). To rationalize this observation we analyzed the parameters that could have an impact on the reactivity: the geometrical parameters for reacting molecules, intermolecular interactions, size and shape of free spaces in crystals and also the substituent effect. It turned out that the role of the substituent effect is important and should be considered during the studies of reactivity of cinnamic acids in crystals.

References:

[1] Galica, T. et al. (2018). Cryst. Growth Des. 18, 1636−1644.

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