L-SWITCH: towards tailor-made molecular switches for specific applications – understanding of transition-metal complexes with ambidentate ligands.

One of main goals of chemistry and physics is to develop new materials that are able to respond rapidly and reliably to changes in a local environment, and send out signals that let us know what is happening. Hence, stimuli-responsive materials, which change their properties under the influence of external factors, have been attracting increasing attention over the years. This is due to their potential wide applications as sensors, catalysts, optoelectronic switches, storage devices, *etc*. It is, thus, of great importance to deeply understand the phenomena behind the desired properties of such materials at the molecular level and sensibly control them, so as to apply this knowledge to design materials with particular properties across all the size scales from molecules to bulk materials, relevant for specific applications. Since changes of materials' properties are often driven by changes in their structure at the molecular level, crystals constitute convenient model systems to study such processes in the solid state using spectroscopic and crystallographic methods. Especially interesting here are molecular switches based on transition metals (TMs) coordination compounds, in which the metal centre is coordinated by one or more ambidentate ligands. Binding mode of these key moieties can be modified via external stimuli (*e.g.* light, temperature, or pressure), leading to changes in the micro- and macroscopic properties of the compound and resulting material.

In view of the above, the current project is dedicated primarily to investigate the factors crucial for the photo- and pressure-induced switching activity of model representative TM complexes with ambidentate ligands and, thus, understand the structure-property relationships. For that purpose three groups of compounds were selected, *i.e.* (1) square-planar nitrite complexes of Ni, Pd, Pt, or Rh; (2) octahedral nitrite complexes of Ni, Co, Fe, or Ru; (3) modifications of the first two groups with other ambidentate ligands, especially SO_2, but also NO, CN/SCN. The first group of compounds constitutes a continuation of our earlier studies on square-planar nickel nitro complexes with the (*N*,*N*,*O*)-donor ancillary ligands, however, will be extended towards other classes of this kind of compounds, including mainly these with pincer-type supporting ligands. In turn, the second group originates from promising preliminary results obtained for octahedral Ni^{II} (high-pressure-induced molecular switching) and Co^{II} complexes (photoswitching potential at room temperature), both coordinated by multiple nitro groups. Finally, the third group will enable comparison of the effect of various ambidentate ligands, molecular charges, *etc.*, as well as such compounds can exhibit interesting magnetic and spectroscopic properties. This choice of compounds shall facilitate testing of numerous factors that affect, or govern, switching properties of this kind of systems, and also will enable comprehensive investigations of the isomerization reaction mechanism in the case of various compounds and crystal environments. In consequence, such gained knowledge and understanding will strongly contribute to our conscious design of functional materials of this kind with specific properties and switching activity under desired conditions.

During the course of this project a set of transition-metal coordination complexes with various ambidentate ligands will be obtained and comprehensively characterized. We plan to investigate the studied compounds using standard physicochemical methods, as well as various spectroscopic and structural methods. The proposed project consists of several interconnected stages. Its overall scheme is as follows: synthesis and crystallisation → spectroscopic and physicochemical characterisation → (photo)crystallographic and high-pressure experiments → quantum chemistry modelling → understanding of the phenomena → design of novel molecular switches. We believe that the obtained results will provide us with the knowledge indispensable to design molecular switches characterized by desired properties, appropriate for further technological applications.