Probing an excited state of a zirconium coordination compound by multi-wavelength single crystal X-ray diffraction at the synchrotron

Birger Dittrich[1], *Prinson Samuel*[2], *Herbert W. Roesky*[2], *Christoph Jacob*[3]

1. Institut für Anorganische und Angewandte Chemie/Universität Hamburg, Martin-Luther King Platz 6, 20146 Hamburg, Germany
2. Institut für Anorganische Chemie/ Georg-August-Universität Göttingen, Tammannstr. 4, 37077 Göttingen, Germany
3. Theoretische Chemie/Technische Universität Braunschweig, Hans-Sommer-Strasse 10, 38106 Braunschweig, Germany

We have recently synthesized and characterized the new zirconium coordination compound $[Zr(Cl)_2(Cp)(PhC(NtBu)_2)]$ (1), amidinatedichloridocyclopentadienylzirconium(IV). Crystals of high quality – disorder is absent – were grown and we have carried out a series of single-crystal diffraction experiments to study the effect of anomalous dispersion around the Kα edge with tunable wavelengths at the SLS synchrotron on these crystals. The energy around the absorption edge corresponds to a wavelength that is high enough to measure diffraction data to rather high resolution of 0.83 in sin Θ/λ. The result of our experiment are conceptually simple difference electron-density maps. These were obtained by using the tools developed for charge density studies. They show electron-density rearrangements around the zirconium atom in three dimensions and correspond to an excited state of the molecule.

Results are in some way analogous to EXAFS or XANES studies, but provide far more detail, which is so far unprecedented. An important detail in data analysis is that only accurate model phases do allow further detailed visualization of relevant remaining un-modeled electron density; features that remain after conventional independent-atom model refinement, for example using SHELXL, do not permit this. Only structure refinement with an aspherical scattering factor model [1] minimizes residual electron density enough. It is therefore mandatory for successful analysis. We have reported very recently how such refinements [2] can be carried out in a computationally efficient manner by starting from tabulated invariom [3] scattering factors using bond distances to hydrogen atoms contained in the invariom database. Comparison of the experimental results to those of theoretical computations is crucial and is currently being carried out.

We are convinced to have a new analytical tool at hand that is useful and widely applicable,possibly even in a laboratory environment at a later stage. Applications could include catalytically active molecules similar to our zirconium compound, small-molecule biomimetics of metal-containing proteins or even “bioinorganic” macromolecules when these show good scattering power and are not disordered.

References:

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