Challenges and Capabilities of Quantum Crystallography for Locating Hydrogen Atoms in Transition Metal Hydrides

Dr. Magdalena Woińska[1], Dr. Sylwia Pawlędzio[1], Dr. Anna A. Hoser[1], Dr. Michał L. Chodkiewicz[1], Prof. Krzysztof Woźniak[1]

[1]*Biological and Chemical Research Centre, Chemistry Department, University of Warsaw*

magdalena.woinska@uw.edu.pl

Transition metal (TM) hydrides are versatile compounds with multiple applications in catalysis, energy conversion, and the search for hydrogen storage materials or superconductors. Therefore, determining the structure of these compounds with X-ray diffraction is essential for many areas of research. However, this is hampered by the challenges of locating the position of hydrogen with X-rays, which are even more aggravated in the case of hydrogen atoms bonded to a TM atom. Furthermore, collecting high-quality, let alone high-resolution X-ray data, for TM hydrides, is an arduous task. It is also difficult to collect neutron data that could provide reliable information about hydrogen positions. TM hydride complexes are also computationally demanding, which makes them difficult to analyze using quantum crystallographic methods.

Hirshfeld atom refinement (HAR) is a quantum crystallographic method that has been proven to locate hydrogen atoms bonded to light elements with accuracy and precision very close to that of neutron experiments, based on standard resolution X-ray data [1]. In some cases, HAR has been reported to improve the positions of hydrogen atoms in TM-H bonds considerably [1, 2], as compared to the Independent Atom Model (IAM). The goal of this study was to evaluate the capabilities of HAR in terms of establishing the positions of hydrogen atoms, especially in TM-H bonds, and to investigate the influence of different parameters adjustable in the refinement on the final result. The following factors were considered: including interactions with the crystal environment, taking into account relativistic effects, changing the DFT functional used for wave function calculations (B3LYP, PBE, M06-2X), and selecting the basis set. Another aspect considered in the study was the role of treatment of hydrogen thermal motion in HAR. To have a large representation of X-ray structures of TM hydride complexes with a corresponding neutron structure available, 10 structures were selected, in which hydrogen atoms were bonded to heavy elements from periods IV (Fe, Ni), V (Nb, Ru, Rh, Sb) and VI (Os). The 10 compounds were ordered according to the quality of the X-ray and the neutron data and the quality of the refinement performed for each of the structures. This allowed us to observe that for the structures at the top of the ranking, HAR yielded TM-H bond lengths in very good agreement with the neutron values, while decreasing quality caused higher divergence from the neutron bond lengths.

To address the issue of treatment of hydrogen thermal motions in HAR and its impact on hydrogen positions in TM hydride complexes, advanced tools such as SHADE3 or Normal Mode Refinement (NoMoRe) [3] were combined with HAR to estimate H ADPs. The thermal ellipsoids obtained during SHADE3, NoMoRe, HAR, and neutron ellipsoids (Fig. 1) were compared using the similarity index (SI) [4], along with its estimated error. A study of the influence of H ADPs obtained with various methods on hydrogen positions, refinement statistics, and ADPs of non-H atoms was performed. This enabled investigation of the correlation between data/refinement quality and the agreement of the ADPs refined or estimated during HAR or IAM with the neutron ADPs. Furthermore, a high-resolution X-ray structure of a complex containing a Cr-H-Cr bond for which neutron data was collected at a similar temperature [5] was used to investigate the effects of data resolution on hydrogen positions and ADPs. This allowed us to observe that thermal ellipsoids of hydrogen atoms obtained with HAR were in better agreement with the neutron ellipsoids after reducing X-ray data to standard resolution ($2\theta = 50°$). An opposite dependency was observed for non-H ellipsoids, which was more pronounced in the case of IAM than for HAR. Trimming the data also slightly improved the X-H and TM-H bond lengths in the case of HAR, whereas, in the case of IAM, only the TM-H bond lengths were affected. In conclusion, in the investigated good-quality and high-resolution data set, low-resolution data appeared to contain all information about hydrogen atoms required for HAR to locate hydrogen atoms in high agreement with neutron diffraction, even in a bridging position between two transition metal atoms.

{1} Woińska, M., Grabowsky, S., Dominiak, P. M., Woźniak, K. & Jayatilaka, D. (2016). Sci. Adv. 2, e1600192.
{2] M. Woińska, M. L. Chodkiewicz, K. Woźniak, Chem. Commun., 2021, 57, 3652-3655.
{3} A. A. Hoser, A. Ø. Madsen, Acta Cryst., 2016, A72, 206–214; A. A. Hoser, A. Ø. Madsen, Acta Cryst., 2017, A73, 102–114.
{4} Spackman, M. A. Chem. Rev., 1992, 92, 1769–1797.
{5} P. Macchi, D. Donghi, A. Sironi, J. Am. Chem. Soc., 2005, 127, 47, 16494–16504.

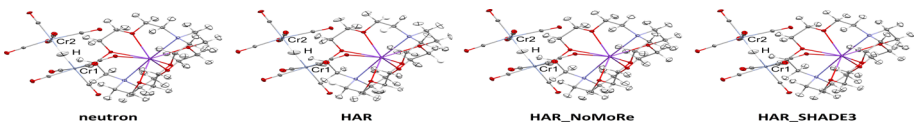

Figure 1. Crystal structures of the chromium hydride complex obtained with various experimental and refinement methods.