

s14.m39.p1 **New Chemical Trends with VIVALDI.** Jacqueline Cole^a and Garry McIntyre^b, ^aUniversity of Cambridge, UK, and ^bInstitut Laue Langevin, France. E-mail: jmc61@cam.ac.uk

Keywords: Neutron; Diffraction; Chemistry

VIVALDI is a Laue-based single-crystal neutron diffraction instrument, newly commissioned at the ILL, Grenoble, France. Its design was based on the forerunner, LADI, which is used at the ILL for diffraction studies of biological macromolecules. Whilst LADI operates via a cold-beam of neutrons, VIVALDI is situated on the end of a thermal neutron guide, thus making it appropriate for studying small molecules with chemical and physical applications.

The conception of VIVALDI came from testing chemical and physical materials when LADI was placed temporarily on a thermal neutron guide at the ILL in 1997. One of these tests is described via the example study of the non-linear optical material, zinc (tris)thiourea sulfate (ZTS). This was a comparative study of results obtained from neutron diffraction data acquired from 'thermal-LADI' and from the high-flux single-crystal neutron diffraction instrument, D9, at the ILL [1]. The nature of the hydrogen positions and hydrogen-bonds were important to establish in this material. The same scientific conclusions were drawn from each experiment, but with LADI showing a gain in efficiency of over a hundred times that over D9 in terms of combined crystal size and data collection time. Thus, such an instrument was proven to be very useful for the determination of hydrogen positions.

The VIVALDI instrument, subsequently constructed, is briefly described, together with an illustration of its performance by example of four chemical studies: the location of a hydride in the Li cage of an organometallic complex [2]; C-H...F hydrogen-bonding in a Zr-based organometallic complex that is important as it is thought to have a role in its catalytic properties [3]; a variable temperature study of the zeolite, YUG, where knowledge of the disordered nature of its water contents are important in assessing its cavity topology and therein its potential to adsorb certain guest molecules [4]; a charge density study of the organic molecule, coumarin [5], a chemical precursor to many laser dyes.

- [1] J. M. Cole, G. J. McIntyre, M. S. Lehmann, D. A. A. Myles, C. Wilkinson, J. A. K. Howard, *Acta Crystallogr.* **A57** (2001) 429-434.
- [2] S. R. Boss, J. M. Cole, R. Haigh, G. J. McIntyre, P. R. Raithby, R. Snaith, A. E. H. Wheatley, *Science* (submitted, 2004).
- [3] S. C. F. Kui, N. Y. Zhu, M. C. W. Chan, *Angew Chemie, Int. Ed.*, **42** (2003) 1628-1632.
- [4] J. M. Cole, G. J. McIntyre, A. Zeidler, to be published.
- [5] J. M. Cole, S. L. G. Husheer, G. J. McIntyre, D. S. Yufit, P. Munshi, G. Row, J. A. K. Howard, to be published.

s14.m39.p2 **Single-Crystal Neutron Diffraction Studies of Transition Metal σ -Complexes.** T. F. Koetzle, A. J. Schultz, J. A. Cowan, M. E. Miller, And X. Wang, *Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, IL 60439, U.S.A.* E-mail: tkoetzle@anl.gov

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This presentation will review a series of neutron structures of σ -complexes that were recently obtained based on data from the IPNS Single Crystal Diffractometer (SCD). Transition-metal σ -complexes are coordination compounds in which two electrons in an X-H σ -bond form a dative bond with a transition metal. This three-center, two-electron bond can be further stabilized by π -backbonding from the metal to the X-H σ^* antibonding orbital. Transition metal σ -complexes are typically reactive intermediates that precede oxidative addition of substrates having an X-H bond. σ -Complexes are, therefore, identified as intermediates in catalytic hydrogenation (X = H), activation and functionalization of hydrocarbons (X = C), hydrosilylation (X = Si), and hydroboration (X = B) reactions. Characterizing the structure and bonding of the intermediate species is important to our understanding of these reactions and to optimizing catalytic processes. Single crystal neutron diffraction can play a critical role here, in σ -complexes, where the positional and thermal parameters of the hydrogen atom in close proximity to a metal are clearly of utmost importance. However, applications have been somewhat hampered at current neutron sources by the need for single crystals larger than 1 mm³. Revolutionary improvements are anticipated with the advent of the new generation of neutron sources, including the Spallation Neutron Source (SNS) that is scheduled to become operational at Oak Ridge, Tennessee, U.S.A., in 2006, where it will become possible to work with crystals approaching the size commonly used in X-ray studies and thus greatly expand the range of materials open to investigation.

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