

The inaugural **2013 ACA Bau Award** was presented to **Thomas Koetzle** by ACA President Cheryl Klein. The Bau Award recognizes exceptional research achievement in neutron diffraction and is named after the late Robert Bau, who made major contributions to the field in the course of his distinguished career at U Southern California. In Koetzle's award lecture, *From Amino Acid Structures to Metal Hydrides: Four Decades of Single-Crystal Neutron Diffraction*, he discussed highlights of the research that he carried out together with his collaborators at Brookhaven National Laboratory's High Flux Beam Reactor (HFBR) and at Argonne's Intense Pulsed Neutron Source (IPNS).

Tom began his presentation by noting that to date less than 1% of reported crystal structures use neutrons. Traditionally, the principal challenges in single-crystal neutron diffraction work have been the requirement for large crystals, along with the somewhat limited number of available neutron scattering facilities. These bottlenecks are now being effectively addressed with a new generation of neutron sources and instrumentation.

The neutron diffraction technique is complementary to x-ray diffraction while offering its own unique strengths. With neutrons the nuclear positions are determined directly, thereby removing any bias that may be introduced in x-ray work due to asymmetries in the electron-density distribution. In neutron diffraction the great majority of isotopes are readily discriminated; H and D, for example, have neutron scattering factors of opposite sign. Neutron scattering cross sections for most of the nuclei are of the same order of magnitude, so that light and heavy atoms are located with comparable precision. In addition the thermal-energy neutrons that are employed in crystallography can be used in spectroscopy to study dynamics along with structure. The neutron's magnetic moment can also be exploited to examine spin densities, for example in molecular magnets. Javier Campo, U Zaragoza discussed molecular magnets in his talk during Session 10.01.

Koetzle's work with neutrons began in the early '70's at Brookhaven where he was mentored by the neutron diffraction pioneer Walter Hamilton. They embarked upon a series of highly precise studies of the structures of amino acids working with a number of visiting scientists, including Mogens Lehmann who later went on to play a leading role in the neutron crystallography program at the Institut Laue Langevin. These amino acid studies were quite a tour de force for their time. They revealed numerous details of the molecular and crystal structures including especially their important hydrogen-bonding interactions. For example in 1972, in their first amino-acid publication, they reported the neutron structure of L-alanine. Lehmann, Koetzle and Hamilton described the three-dimensional network of N-H...O hydrogen bonds in this crystal. They explored barriers to rotation of the methyl and ammonium groups (3.6 and 20 kcal/mol respectively) and discussed implications for hydrogen-bond strength. The hydrogen-bonding interactions in these systems are of great general interest, because they play a central role in molecular recognition in biology.

Following Walter Hamilton's untimely death in 1973, Koetzle carried on the amino acid studies with their collaborators. Also during this time, and subsequently with Dennis Engel, U Durban, Koetzle completed a project that he and Hamilton had initiated to evaluate methods of phase determination based on three-wavelength



neutron anomalous dispersion data for the rare-earth EDTA complex, $\text{Na}[\text{SmEDTA} \cdot 3\text{H}_2\text{O}] \cdot 5\text{H}_2\text{O}$. In his lecture, Tom described how there was quite a bit of interest at the time in what was essentially a neutron forerunner of the fabulously successful Multiple Anomalous Dispersion (MAD) x-ray phasing techniques that ultimately were to revolutionize macromolecular crystallography at synchrotrons. While the experimental measurements for SmEDTA proved to be too time consuming for the neutron application to be feasible in practice, primarily because of the extremely high neutron capture absorption cross section that goes hand-in-hand with samarium anomalous scattering, the Brookhaven study *did* show that highly accurate phases could be obtained for this acentric crystal. Using the raw phases calculated to 2Å resolution, the majority of the hydrogen atoms were readily located. The structure itself is quite challenging, with disordered lattice waters along with sodium cations and nine-coordinate SmEDTA·3H₂O anions.

As described by Tom, the second major theme of his work at Brookhaven was a series of studies of transition-metal hydride complexes that established the details of bonding of hydrogen to metals in these systems. This work was initiated in the mid '70's with Bob Bau and members of Bau's research group. The Brookhaven-USC collaboration, which in all spanned some 25 years and resulted in more than 40 publications, also included a number of studies utilizing H/D substitutions to confirm the absolute stereochemistry of enzymatic reaction products. The hydride work established precise M-H distances for hydrogen in a wide variety of bonding environments: terminal, μ_2 -bridging, μ_3 -bridging, etc., and showed, for example, how the M-H distance increases with increasing H coordination number. Tom described some of the particularly interesting hydride structures, including $(\text{H}_2\text{Rh}_{13}(\text{CO})_{24})^{3-}$ with its two five-coordinate hydrides in square-pyramidal geometry and $\text{HCo}_6(\text{CO})_{15}^-$ with its six-coordinate interstitial hydride in the octahedral $\text{Co}_6(\text{CO})_{15}$ cluster. He also discussed a series of studies of complexes with bound η^2 -dihydrogen ligands,

also known as “non-classical” hydrides, of the type that were first prepared by Gregory Kubas at Los Alamos. This work, which was carried out with collaborators including Alberto Albinati, U Milan, Juergen Eckert, Los Alamos, and Tom’s long-time colleague the late Richard McMullan of Brookhaven, allowed for the quantitative determination of the elongation of the H–H bond in these important sigma complexes, which may be viewed as prototypes for the activation of dihydrogen in many catalytic systems. Incoherent inelastic neutron scattering spectroscopy was also used to confirm the critical role of metal π -electron back donation in stabilizing these non-classical hydride systems.

When the Brookhaven HFBR was closed in the late 90’s, Tom moved to Argonne’s IPNS and continued his work there for a decade with Arthur Schultz and members of Schultz’s group. Tom described a parametric study from this period that was performed over a range of temperatures for tetraacetylene (TAE). TAE is an interesting crystal with a short intramolecular O–H...O hydrogen bond that shows a systematic displacement of its H atom with temperature and may serve as a model for proton transfer. The TAE study, with neutron work carried out by Paula Piccoli at Argonne, also included a precise charge-density analysis at 20 K with Alan Pinkerton and collaborators from U Toledo probing the electron distribution in the short hydrogen bond.

Tom concluded his Bau Award lecture by very briefly reviewing some of the recent developments at two of the newest generation neutron sources. For example, at J-PARC in Tokai, Japan, the iBIX single-crystal diffractometer at the Materials and Life Science Facility has recently been used to study the structure of an interesting analog for the active site of the enzyme [NiFe] hydrogenase. At the Oak Ridge Spallation Neutron Source (SNS), the TOPAZ single-crystal diffractometer has recently been added to the user program, and the SNS has just accepted its first round of TOPAZ experiment proposals. TOPAZ and iBIX are just two among a number of new instruments that are making it more convenient to use considerably smaller crystals, while keeping neutron beam time down to no more than a few days.

Martha Teeter (adapted & revised by Tom Koetzle)