Lawrence F. Dahl

# BIOGRAPHICAL

A Biographical Memoir by John F. Berry

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NATIONAL ACADEMY OF SCIENCES

# LAWRENCE FREDERICK DAHL

June 2, 1929–March 20, 2021 Elected to the NAS, 1988

Lawrence Frederick Dahl contributed enormously to our understanding of the solid-state structures, stereochemistry, bonding, and synthesis of transition metal carbonyl cluster compounds. His work to elucidate the structures of simple metal carbonyl compounds by single-crystal X-ray diffractometry provided clarity to controversial structural proposals, correct identification of a number of compounds that were previously ill-characterized, and discoveries of unprecedented and often surprising structures. After early work with simple metal carbonyls, Larry systematically pursued related compounds with additional halogen, chalcogen, pnictogen, and phosphine ligands. Larry continually pushed the frontier of crystallography, and his later work included structural characterization of high-nuclearity cluster compounds, up to 165 metal



By John F. Berry

atoms, that provide the most detailed atomic-scale pictures of metal nanoparticles.

In addition to his outstanding research accomplishments, Larry was a dedicated teacher and mentor. He taught introductory freshman chemistry at the University of Wisconsin– Madison (UW–Madison) for nearly fifty years, impacting the lives of well over 10,000 students. His enthusiasm for chemistry was infectious, and he encouraged many of the students that he interacted with to continue studying chemistry. Nearly 100 graduate students completed doctoral work with Larry, and he generously served as an unofficial mentor to many others. He was never shy to share the secret to his success. He humbly attributed his accomplishments to the hard work of his coworkers and to the Goddess Fortuna.

## **Academic Life**

Larry Dahl was born June 2, 1929, in Chicago, Illinois, to Lawrence G. Dahl and Anna Stuessy Dahl. In Larry's early high school and college education, he did not consider himself an especially good student but enjoyed playing piano, ballroom dancing, and



High school graduation photo. (Dahl family photo.)

playing ping-pong. It was as a graduate student that Larry discovered his penchant for laboratory work and began to excel in research.

Larry received a B.S. in 1951 from the University of Louisville and a Ph.D. in 1956 from Iowa State University, where his advisor was Robert E. Rundle. Rundle was an expert in X-ray crystallography, having obtained his Ph.D. in the use of this technique under the tutelage of two-time Nobel laureate Linus Pauling at the California Institute of Technology (Caltech). Larry soon became proficient in crystallographic techniques, which remain the most powerful analytical methods for solid-state structure determination with atomic scale resolution. Larry's dissertation<sup>1</sup> contained three structural studies: complete structural studies of  $Mn_2(CO)_{10}$  and  $Re_2(CO)_{10}$  and a significant but partially complete analysis of  $Fe_3(CO)_{12}$ . While working on his Ph.D. in Rundle's lab, Larry met June Lomnes around 1953, and the two were

married in 1958. During a postdoctoral year working at Ames Laboratory in Iowa, Rundle was invited to give a lecture by the UW–Madison Department of Chemistry but couldn't attend due to an illness. He instead arranged for Larry to travel to Madison to give a lecture in his stead. This lecture so impressed Farrington Daniels, who was the department chair, that Larry was hired as an instructor in September 1957. He was hired to teach general chemistry, as there was no inorganic chemistry program at UW– Madison at the time. That changed when Larry and his colleague Bob West prevailed in convincing the rest of the faculty that their "inorganic" research was just as strong as the other research areas in the department.

In 1959, Larry was hired as an assistant professor and was awarded \$3,000 from UW– Madison to start his research program. He used the funds to purchase a Weissenberg camera and a precession camera and set to work collecting X-ray diffraction data using a hand-me-down X-ray generator. In the early days, Larry's group analyzed crystalline samples provided by other researchers, but the department soon set up a wet lab in which Larry's coworkers worked their synthetic magic. Larry advised his students to "work hard, and play hard: If the Goddess Fortuna is in the lab, then lock the door and work as long as She is there. If She is not in the lab—take some time off to do other things." Larry embodied this mentality, as he was often found working late into the night, but he would

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also be willing to challenge any student to a ping-pong match. These were high-stakes matches: Larry said that he would award a Ph.D. to any student who won against him. In the rare instances when Larry did lose a match, a rematch quickly followed so that Larry could revoke any premature degree.

After promotion to associate professor in 1963, his Ph.D. advisor R. E. Rundle passed away suddenly at the age of only forty-seven. Larry was approached by Iowa State with an offer to become Rundle's successor. But Larry chose to remain at UW–Madison and was tenured and promoted to professor in 1964. In 1978, Larry was honored with a named professorship, and he chose to be named the R. E. Rundle Professor of Chemistry. In 1991, he was named a Hilldale Professor, which is UW–Madison's highest honorific title. When I first met then-75-year-old Larry in 2005, his first words were: "I don't plan to retire—I'm having too much fun!" But Larry did retire in 2008, although he remained active. He generously volunteered to teach general chemistry for one last semester, and in 2009, Larry traveled to and from Grinnell, Iowa, to give a series of crystallography lectures at Grinnell College. Larry's last classroom lecture was a guest lecture in the graduate crystallography class in 2018. Until 2018, Larry maintained a research lab with research scientist Evgueni Mednikov and his last Ph.D. student, Jeremiah Erickson, who graduated in 2013.

# Metal Carbonyls—A Sixty-Year Saga

Larry's seminal early work on transition metal carbon monoxide cluster compounds remains highly cited and provides textbook examples to illustrate the principles of electron counting and cluster metal-metal bonding. Furthermore, many of the compounds that were novel at the time are now commercially available and used routinely as starting materials. A structure of one such compound that held special importance for Larry was that of triiron dodecacarbonyl,  $Fe_3(CO)_{12}$ , which he started working on in 1952. Larry's dissertation includes a meticulous analysis of the X-ray diffraction pattern in Patterson space. At the time, the analysis was done by hand and took years of work; with today's modern software it is done with the click of a mouse. Larry liked to remind his coworkers that he learned crystallography in the BC era: "before computers." Diffraction intensities were determined by eye from X-ray–exposed film.

The major scientific conundrum about  $Fe_3(CO)_{12}$  was the arrangement of the three metal atoms. Was it a linear trinuclear structure, triangular, or something completely unsymmetric? Preliminary diffraction data on the compound was claimed to be consistent with

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a linear, trinuclear structure because the  $Fe_3(CO)_{12}$  molecules were required by the space group symmetry to occupy an inversion center. Larry's deeper analysis found a hexagon of six half-occupied iron atoms, disordered in a "star-of-David" pattern. Thus, Larry was able to report a triangular structure but could not report full structural details because of the metal atom disorder, and thus the structure remained controversial. Interestingly, an intrepid Ph.D. student at Harvard University named F. Albert Cotton was also trying to determine this structure at the time. Larry and Cotton corresponded but did not collaborate, as Larry indicated that Cotton was proposing an incorrect structure. After this initial interaction, Larry and Cotton developed a lifelong mutual respect for one another, though they never again worked on the same problems. In 1965, now at UW–Madison, Larry and J. F. Blount brilliantly circumvented the metal atom disorder problem through structural analysis of the hydrogen-bond-locked  $[HFe_3(CO)_{11}]^-$  anion, and a new dataset allowed for full refinement of the disordered  $Fe_3(CO)_{12}$  structure. It was reported by Larry and C. H. Wei in 1966:

All further speculation concerning the probable structures of  $Fe_3(CO)_{12}$ and  $Co_4(CO)_{12}$  in the solid state can be laid to rest; the structures of these two important transition metal carbonyls have been ascertained from three-dimensional X-ray investigations.

Larry gives a detailed account of these and other results on the  $Fe_3(CO)_{12}$  structure in his paper in the *Journal of Cluster Science* entitled "Sixty-Year Saga (1952–2013) of the Solid-State Structure of Triiron Dodecacarbonyl."<sup>2</sup> He also references other work from his lab on metal carbonyls:

So while LFD continued his efforts at UW–Madison to elucidate the solidstate structure of  $Fe_3(CO)_{12}$  several of his first graduate students utilized a high-pressure CO apparatus to prepare samples of other known polynuclear metal carbonyls for crystallographic/spectroscopic analyses. Early work included: (1) that the previously reported  $Os_2(CO)_9$  and  $Ru_2(CO)_9$ were incorrectly formulated and are in fact analogous triangular osmium and ruthenium  $M_3(CO)_{12}$  clusters (M = Os, Ru); a detailed crystal structure of  $Os_3(CO)_{12}$  showed it to possess a metal triangle of pseudo- $D_{3h}$ symmetry without bridging carbonyl groups; (2) that the previously reported  $Rh_4(CO)_{11}$  (based mainly upon elemental analysis) is actually  $Rh_6(CO)_{16}$  which has an octahedral  $Rh_6$  core with 12 terminal CO and 4 triply bridging CO ligands that ideally conform to  $T_d$  symmetry; and (3) the

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structural discovery in 1962 of the penta-coordinated square-pyramidal carbido atom in  $Fe_{5}(\mu_{5}-C)(CO)_{15}$  which initially demonstrated that discrete transition metal clusters can incorporate an interstitial carbon atom.

The carbido complex was particularly surprising, as the tetravalency of carbon was strict dogma in organic chemistry. Larry recalled presenting this result at a conference and being questioned by one of the attendees: "How can an organic carbon atom form five bonds?" Without missing a beat, Larry responded: "This isn't an organic carbon atom. It's an inorganic carbon atom!" This inorganic carbido structure was the first example of hypervalent carbon bonded to transition metals, but it was not the last. Notable are (1) five- and six-coordinate carbido atoms surrounded by gold atoms, reported in the 1980s by Hubert Schmidbauer's group at Technische Universität München, with trigonal bipyramidal and octahedral geometries, respectively, and (2) the six-coordinate, trigonal prismatic geometry of the central carbido atom, identified in 2011, in the FeMo cofactor of the nitrogenase protein, which is the active site responsible for natural nitrogen fixation.



Larry at a group outing. (Dahl family photo.)

## **One-Electron Bonds and Bent, Protonated Metal-Metal Bonds**

As an academic grandchild of Linus Pauling, Larry had a natural interest in the nature of chemical bonds. Metal carbonyl chemistry provided numerous examples of unusual bonding situations, from the simple unsupported electron-pair Mn–Mn and Re–Re bonds in  $Mn_2(CO)_{10}$  and  $Re_2(CO)_{10}$  from Larry's thesis work to an analogous unsupported Co–Co bond in the  $[Co_2(CN)_{10}]^{4-}$  anion, which he reported contemporaneously with University of California, Berkeley professor Ken Raymond in 1972, to delocalized metal-metal bonds in larger clusters. In the 1960s and 1970s, ideas such as molecular orbital (MO) theory were being applied vigorously to metal-metal bonded systems, and Larry sought "operational tests" of these ideas in his lab's synthetic work in projects that he dubbed "experimental MO theory." For example, in 1970 Larry published a paper in the *Journal of the American Chemical Society* describing the effect of one-electron oxidation of the thiolate-bridged dimer Fe<sub>2</sub>Cp<sub>2</sub>(CO)<sub>2</sub>(SCH<sub>3</sub>)<sub>2</sub>, finding a contraction of the Fe–Fe distance by 0.46 Å. This result was significant in that it indicated that the electron was removed from an Fe–Fe antibonding orbital and that the resulting monocation contained a one-electron metal-metal bond.

A series of three papers in the *Journal of the American Chemical Society* in 1966, 1970, and 1977 describe the unusual structure of the  $[Cr_2(CO)_{10}(\mu_2-H)]^-$  anion. Initially, the anion was described as having a Cr–H–Cr three-center, one-electron-pair bond, and a linear, symmetric structure was deduced. In comparison to the structure of the  $[Cr_2(CO)_{10}]^{2-}$  ion, isoelectronic to  $Mn_2(CO)_{10}$ , the  $[Cr_2(CO)_{10}(\mu_2-H)]^-$  ion was described as containing a linearly protonated metal-metal bond. The protonation involved a contraction of the Cr–Cr distance by 0.44 Å. Recognizing the difficulty of accurately determining the positions of hydrogen atoms in close proximity to metals by X-ray diffraction. Larry's group, in collaboration with Jack Williams at Argonne National Laboratory, performed a neutron diffraction study that located the hydrogen atom unambiguously, revealing a disordered, bent symmetric Cr–H–Cr bond.

## **High-Nuclearity Clusters**

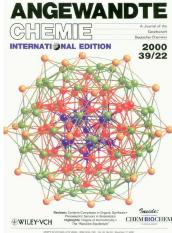
In a 1986 paper in the *Journal of the American Chemical Society*, Larry reported a new breakthrough, in which reaction of the known  $[Ni_6(CO)_{12}]^{2-}$  ion with  $Rh_2(CO)_4Cl_2$  produced a high-nuclearity metal carbonyl cluster possessing an 11-atom  $Rh_5Ni_6$  core. As a harbinger of things to come, "clusterification" reactions and building of larger high-nuclearity compounds now became major goals of Larry's research team. One key to the discovery of these new types of clusters seemed to be the use of more than one metal in the synthesis. After the initial  $Rh_5Ni_6$  report came a  $Au_6Ni_{12}$  cluster with an 18-vertex core made up of five face-fused octahedra, a  $Pd_{33}Ni_9$  cluster with several closely packed layers of metal atoms, 38-atom  $Au_6(Pd,Ni)_{32}$  clusters with partial solid-solution alloying, and many others.

Concurrent with this heterometallic work, it was recognized that the elements Ni, Pd, and Pt (though especially Pd) could produce homometallic high-nuclearity clusters on their own without heterometals. A mix of CO and phosphine ligands led to the discovery of a large family of high-nuclearity clusters. Some multi-nuclear clusters could be synthesized on a large enough scale to serve as starting materials for even larger clusters. Particularly important is the family of Pd<sub>10</sub>(CO)<sub>12</sub>(PR<sub>3</sub>)<sub>6</sub> clusters, obtained by Evgueni Mednikov in Russia in early 1980s. The crystal structure was established for Pd<sub>10</sub>(CO)<sub>12</sub>(P(butyl)<sub>3</sub>)<sub>6</sub> by Yuri Slovokhotov and Yuri Struchkov in 1981 and soon after for two strikingly different Pd<sub>23</sub> as well as Pd<sub>34</sub> and Pd<sub>38</sub> clusters obtained from Pd<sub>10</sub>(CO)<sub>12</sub>(PEt<sub>3</sub>)<sub>6</sub> (1986–1987). Larry began an extremely fruitful collaboration with Mednikov, attracting him to join the UW–Madison Department of Chemistry as a research scientist in 2000.

By the early 1990s, Larry's research on high-nuclearity clusters was stymied by limitations in crystallographic instrumentation. At the time, crystallographic data collection was a slow and arduous process, as point-detector diffractometers measured the intensities of diffraction spots one at a time. Measurements required crystals to be stable over a long period of time, which could be weeks for crystals of large molecules. One day, Larry received a phone call from his former student Charles Campana, who was working at Bruker Advanced X-ray Solutions (AXS) just outside Madison. Bruker was developing what would quickly become a huge breakthrough in diffractometry instrumentation: a charged-coupled device (CCD) area detector system, hearkening back to film techniques but with computer-aided intensity determination. The area detector systems cut down measurement times to hours instead of days. Larry was keen to try out Bruker's new toy—he brought five sets of crystals with him to the Bruker AXS facility. Four crystals did not diffract, and if the fifth did not diffract, then Larry said he would have retired. But the fifth crystal did diffract and produced a rich diffraction pattern clearly indicative of a large molecular structure.

Thus, with the advent of CCD area detector diffractometry technology, in the period between 1990–2016, Larry's group reported mixed CO/phosphine-ligated palladium clusters containing 12, 16, 23, 29, 30, 35, 37, 39, 52, 54, 55, 59, 66, 69, and even 145 palladium atoms. The Pd<sub>145</sub> cluster was a huge discovery, as it provided the first atomic-scale picture of a semi-spherical Pd nanoparticle. For the publication of this compound, Larry would only agree to submit his paper to a journal that agreed to feature the Pd<sub>145</sub> cluster on its cover. Indeed, that's what happened, and the cover art is shown as a figure to the right. I was a Ph.D. student with F. A. Cotton at the time when this structure was reported. Cotton said that he would have given his right pinky finger to have discovered this beautiful molecule!

As beautiful and groundbreaking as the  $Pd_{145}$  cluster was, the *pièce de résistance* in the high-nuclearity cluster field was yet to come: a mixed Pd/Pt cluster of icosahedral symmetry with a shell-growth pattern containing a total of 165 metal



Cover art from Angewandte Chemie displaying the structure of the Pd145 cluster. (Copyright © 2000, John Wiley and Sons.)

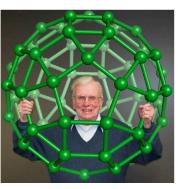
atoms with a completed pentagonal dodecahedron as a fourth shell. This discovery was reported in the *Journal of the American Chemical Society* in 2007. The photo below shows

Larry trapped inside of the third shell (not to scale!). Larry wrote about this remarkable research program in his last post-tenure review document:

Our research has emphasized the highly versatile nature of palladium as a unique transition metal in readily forming a remarkable array of highly condensed carbonyl/phosphine clusters with either icosahedral-, ccp-, or mixed ccp/hcp-based metal core arrangements. Our research also has considerable general interest since palladium has special commercial importance in that it forms exceptionally efficient mono- and bimetallic catalysts for organic reactions. Another major outcome of our research is that the unprecedented metal-core architectures, which are being uncovered in our laboratory for ligated monometallic, bimetallic and trimetallic clusters, have important stereochemical implications as model systems concerning multitwinned structures and growth patterns of much larger ligated and nonligated palladium and heteropalladium nanoparticles and hence are of relevance in both Nanoscience and Nanotechnology.

## Larry's "Better Half"

Larry could not take a compliment on his achievements without also extoling those of his wife, June Dahl. June grew up outside of Saint Paul, Minnesota, and attended



Larry, incarcerated inside one of the shells of the (Pd,Pt)<sub>165</sub> cluster. (Department of Chemistry, University of Wisconsin – Madison photo.)

Macalester College and then Iowa State University. June was the only female student in her undergraduate and graduate chemistry classes and successfully earned a Ph.D. in physical chemistry despite active discouragement by some academics from pursuing science on the basis of her gender. She moved with Larry to UW-Madison and provided valuable support for Larry's research program in the early days, including helping to edit papers. At UW-Madison, June became first a postdoc and then a lecturer in the Department of Pharmacology, and eventually was appointed as a part-time faculty member in the Department of Neuroscience. She insisted on a part-time appointment because she and Larry were raising three children. She broke ground in becoming the first part-time assistant professor to earn tenure at UW-Madison. Currently, June is Professor Emerita in Neuroscience, and her area of expertise is pain management. In 1977, she was appointed by the governor



Larry and June Dahl, ca. 2009. (Dahl family photo.)

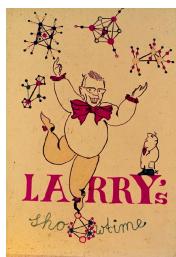
of Wisconsin to serve on the state's Controlled Substances Board, and she aided in developing the current standards for assessing pain in cancer patients through her work on the Wisconsin Cancer Pain Initiative. Whenever Larry accompanied June to a national conference where she was delivering an invited talk, he preferred being introduced as Professor June Dahl's husband, Mr. Larry Dahl. He was immensely proud of June and her professional accomplishments.

## **Lecture Style**

Larry's lectures on chemistry and crystallography were legendary. Conference and symposium organizers learned to always schedule a lecture from Larry at the end of a session to account for the highly probable event that Larry's lecture would run longer than anticipated. No

matter the time allotted, it was never enough to contain Larry's endless enthusiasm for structural chemistry. In the classroom, the stentorian bells that announced the end of the

class period meant little to Larry, who continued to lecture in what he called "reciprocal time" until he had no more to say and was coated from head to toe in chalk dust. For research presentations, he presented so many structural results that the "Dahl unit" was invented to quantify the unusually high number of slides presented in his lectures. Initially, the Dahl unit indicated a full slide carosel, which held 80 slides; some of Larry's lectures required one and a half or two Dahl units. For Larry's 80<sup>th</sup> birthday in 2009, the UW–Madison Department of Chemistry held a celebration in his honor. At this "Geburtstag" party (Larry was fond of peppering his speech with German words on occasion), Larry was presented with a proclamation from the Madison mayor and a cake with the inscription "Happy Birthday Larry! 80 Years = 1 Dahl Unit."



Whimsical reinterpretation of one of Larry's lectures on structural chemistry.

# **Impact and Legacy**

Larry mentored nearly one hundred Ph.D. students during his career, in addition to working with a large number of postdoctoral associates, graduate and undergraduate students, and visiting faculty. Always generous with his time, it was not uncommon for Larry to serve as an unofficial advisor to graduate or undergraduate students working in other research groups as well. He never turned down the opportunity to read a manuscript for one of his colleagues, making corrections to both science and grammar. Larry was an exceptional writer who described his chemistry thoroughly. His papers are distinguished by a characteristic writing style and excellent command of the English language. In his articles, Larry's students and coworkers were listed as the lead authors, even when the majority of the writing and manuscript editing was performed by Larry himself. Larry was a scholar in the truest sense of the word: he did not just read papers in his field; he also read papers cited in those papers, and the papers cited therein.

Larry's contributions to teaching include the creation of a rigorous graduate course in chemical crystallography and teaching freshman chemistry for nearly fifty years to at least 10,000 undergraduate students. In connection with his research, he served on the editorial boards of numerous journals in his field, including *Chemical Reviews, Journal of Physical Chemistry, Journal of Organometallic Chemistry, Journal of Coordination Chemistry,* and the *Journal of Cluster Science.* 

Larry's research resulted in over 300 publications and had a profound impact on the field of inorganic chemistry, an accomplishment that was recognized by his election to the National Academy of Sciences in 1988. Other noteworthy accolades include his election as a Fellow of the American Academy of Arts and Sciences (1992) and the New York Academy of Sciences (1975) and his receipt of the American Chemical Society Award in Inorganic Chemistry (1974), the Willard Gibbs Medal (1999), the Pioneer Award of the American Institute of Chemists (2000), the F. Albert Cotton Award in Synthetic Inorganic Chemistry (2010), and his election as a Fellow of the American Crystallographic Association (2014). In 1994, he received the University of Wisconsin Hilldale Award from the Division of Physical Sciences. Larry delivered a large number of prominent lectureships, including the Paolo Chini Lectureship endowed by the Italian Society of Chemistry, the J. C. Bailar Jr. Lectures at the University of Illinois-Urbana Champaign, the Fred Basolo Lectures at Northwestern University, and the Sir Ronald Nyholm Lectureship sponsored by the Royal Society of Chemistry in the United Kingdom. Larry was appointed a "Kentucky Colonel" by the governor of Kentucky in 1982. A decade

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later, he received the first Alumnus Award from the College of Arts and Sciences at the University of Louisville and an Honorary Doctorate Degree from the University of Louisville.

An archetypal academic scientist, Larry positively affected the lives and influenced the careers of an innumerable number of students and colleagues, offering support and words of encouragement in addition to scientific advice. He was always sincerely interested in people and was extremely generous with his time. An accomplished writer with a long list of scientific publications, Larry credited the Goddess Fortuna in one of his papers for the good luck in chemical synthesis and crystallization that she brought his research group over the years. Larry knew how to enjoy life, had an unfailingly positive attitude, and remained enthusiastic about science to the very end. He was preceded in death by his son, Christopher Dahl, and is survived by his wife June, sons Lawrence and Eric, and grandson Lawrence Samuel. He was a brilliant researcher, a thoughtful advisor, a wonderful colleague, and a dear friend.

## Acknowledgments

I am grateful to Larry's family, in particular June Dahl and their son Lawrence Dahl, for sharing their recollections. Many thanks to Ilia Guzei, Ariel Andrea, and Kristi Heming for their help in assembling materials for this manuscript and sharing their recollections. Evgueni Mednikov, Jeffrey Petersen, and Chuck Campana are gratefully acknowledged for reviewing an early draft of this manuscript. Last, but certainly not least, I must acknowledge the influence and inspiration of G. Fortuna.



# **Principal Awards and Honors**

1963-1965 Sloan Fellow

- 1969 Guggenheim Fellow
- 1972 American Chemical Society Award in Inorganic Chemistry
- 1975 Elected Fellow of the New York Academy of Sciences
- 1978 Named R. E. Rundle Professor of Chemistry
- 1982 Appointed as a Kentucky Colonel
- 1985 Senior Alexander von Humboldt Fellowship
- 1988 Elected Member of the National Academy of Sciences
- 1991 Honorary Doctorate, University of Louisville
- 1991 Named Hilldale Professor of Chemistry
- 1992 Elected Fellow of the American Academy of Arts and Sciences
- 1999 J. Willard Gibbs Medal
- 2000 Pioneer Award of the American Institute of Chemists
- 2010 F. Albert Cotton Award in Synthetic Inorganic Chemistry
- 2014 Fellow of the American Crystallographic Association

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