BIOGRAPHICAL
MEMOIRS

JOHN D. CORBETT

March 23, 1926–September 2, 2013
Elected to the NAS, 1992

A Biographical Memoir by Gerd H. Meyer

JOHN D. CORBETT, Distinguished Professor of Chemistry at Iowa State University and Senior Scientist at the Ames Laboratory, was a molten-salt, physical chemist mutated into an inorganic solid-state and materials chemist. As he wrote in many of his papers, "first comes the synthesis" to discover the unimaginable. Indeed, his first studies were concerned with the solubility of metals in their molten salts and led to the discovery of, then unimaginable, rare-earth and transition metal clusters with and without interstitial (endohedral) hetero atoms. Together with groundbreaking discoveries of novel homo and hetero polycations and -anions and main-group metal fullerenes, he entered the area of polar intermetallics uncovering, finally, new quasicrystals and their approximants. Among these, he especially admired the beauty of (anionic) gold partial structures in some of these compounds. During his 60 years of research and teaching at Iowa State University, John D. Corbett expeditiously developed into a world-renowned leader who influenced his and the next generation of inorganic solid-state chemists and materials scientists.

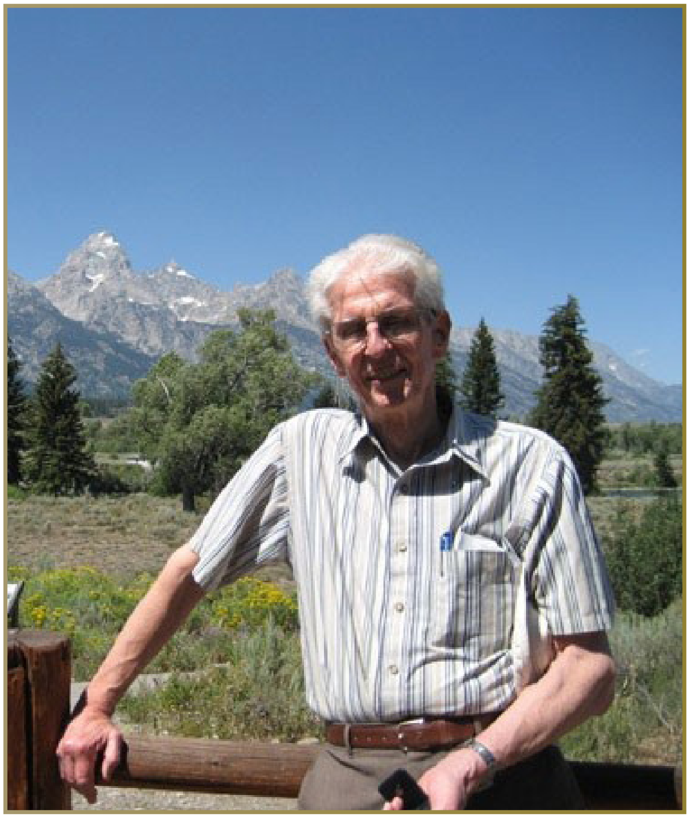

Figure 1 John D. Corbett in front of the Grand Teton Mountains, Wyoming, 2006. *Courtesy of Julia B. Corbett.*

EARLY LIFE AND EDUCATION

John Dudley Corbett was born on March 23, 1926, in Yakima, Washington, the son of Alexander Hazen and Elizabeth Dudley Corbett. His early education was in the elementary schools of Yakima. He graduated from Yakima Senior High School in 1944 and enlisted in the United States Navy. He then attended North Dakota State Teachers College and the University of Wisconsin under the V-12 Navy College Training Program and Naval Reserve Officers Training Corps and was discharged from service in 1946.

He entered the University of Washington in 1946 and graduated with a bachelor of science in chemistry in 1948. On August 7, 1948, he married Irene Lienkaemper of Coquille, Oregon. He remained at the University of Washington for graduate work and was an E. I. duPont de Nemours research fellow for the 1950–51 academic year and later was a teaching fellow in chemistry. He is a member of Phi Lambda Upsilon and an associate member of Sigma Xi. He completed his Ph.D. on August 22, 1952, with a thesis

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entitled "Anhydrous Aluminum Halides and Mixed Halide Intermediates."

ACADEMIC CAREER

In a stroke of genius, Frank H. Spedding, then-director of the Institute for Atomic Research at Iowa State University and the Ames Laboratory of the United States Atomic Energy Commission, hired the twenty-six-year-old John D. Corbett, without having interviewed him in person, as an associate chemist at his laboratory. The university's Department of Chemistry co-hired him as an assistant professor at the same time.

When John accepted the dual appointment as faculty member and Ames Lab scientist in 1952, he and Irene hauled their belongings in their car some 1,800 miles from Seattle to Ames, rented an apartment, and soon started a family. Their three children were all born and raised in Ames: Scott (1953–2009), Julia (1955) and Jim (1960).

Irene had earned a bachelor's degree in home economics with a minor in art from the University of Washington and had started her own career at the Bon Marché department store in Seattle. But when John was hired at Ames, Irene noted, "That was the end of my designing career for the moment."[1] Just for the moment! She became active in setting up and managing a mental health center at Iowa State and devoted all her free time to "playing with yarn [weaving on a double-beam loom] instead of weeds [dried plants],"[2] creating wall sculptures. Irene wove and designed women's clothing that she sold in Ames and even in Minneapolis and San Francisco and had several art exhibitions of her own in Ames. She enjoyed traveling with her husband during sabbaticals in Europe. There were several occasions with longer stays in Denmark, England, and Germany, especially in 1979 and 1986.

In 1963, John was promoted to full professor and senior chemist in the Ames Laboratory, and he served as department chair from 1968 to 1973. In 1974, he was named program director of materials chemistry for the Ames Laboratory, serving until 1978. In 1983, he received Iowa State University's highest honor for faculty by being named a distinguished professor. During his academic career, he mentored forty-one Ph.D. students, fifteen master's degree students, and seventy-two postdoctoral students. He published almost 500 articles in peer-reviewed journals and presented at more than 330 invited seminars around the world. John was a visiting researcher and professor at the Max Planck Institute for Solid State Research in Stuttgart and also was a visiting scholar at the Technical University of Denmark, Oxford University, and Justus-Liebig-Universität, Giessen.

In 2000, John took a half-time position at Iowa State University—no formal teaching, no graduate students—to have more time to manage an active and vigorous research program, discovering new compounds, as he noted, "that one stumbled upon during experiments designed with plausible but incorrect or naïve ideas regarding possible compounds or structural targets." He continued mentoring three postdoctoral students with support from the U.S. National Science Foundation and the U.S. Department of Energy (DOE) until Monday, August 26, 2013, his last day in the laboratory. The week before, he had submitted two papers and intended to prepare an invited lecture for a meeting at Lviv, Ukraine, that September entitled "A Substantial New Gold Chemistry among Polar Intermetallic Phases." Gold had become the new wonder element, and his eyes sparkled with joy when he started talking about the beauty of gold partial structures in many intermetallic phases (see the section on his research).

In 2007, John established an endowed professorship at Iowa State University in his name. The professorship was designed to reward outstanding faculty members and provide the flexibility to pursue avenues of research that are not necessarily attractive to funding agencies.

RESEARCH INTERESTS

During the Manhattan Project, Spedding and Harley Wilhelm and their teams solved the problem of producing pure uranium metal on a large scale by reduction of uranium halides with alkaline-earth metals (such as magnesium and calcium) in sealed refractory metal containers (niobium, tantalum).[3] After World War II, Spedding and associates gradually moved away from transactinide research and established the true legacy of the Ames Laboratory (now the Ames National Laboratory), the separation of the rare-earth elements, production of spectroscopically pure rare-earth metals and compounds, and applied research of rare earths, such as catalysts, magnets, and conductors.

Corbett, trained as a molten-salt physical chemist, immediately saw the opportunities, and his insatiable curiosity came into full action. He merged his background in fused (molten) salts with the equipment and knowledge of the inorganic chemistry of pure metals produced in the Ames Lab. His approach was to first learn what molten salts would do with transition and post-transition metals. The rare-earth metals, available in high purity at the Ames Lab, were the special target of his research, through which lower valent ("reduced") halides emerged, such as PrI_2 and Pr_2I_5, the mysterious $PrCl_{2.31}$, and $NdCl_{2.27}$ and Ho_5Cl_{11}. The "wonder element" turned out to be gadolinium. There was, on the one hand, GdI_2, a compound with a Curie temperature higher than that of Gd metal and, on the other hand, the composition/temperature phase diagram of $GdCl_3$/Gd revealed the "eighth wonder of the rare earth world," gadolinium sesquichloride, Gd_2Cl_3, a black salt with a metallic luster.[4] At that

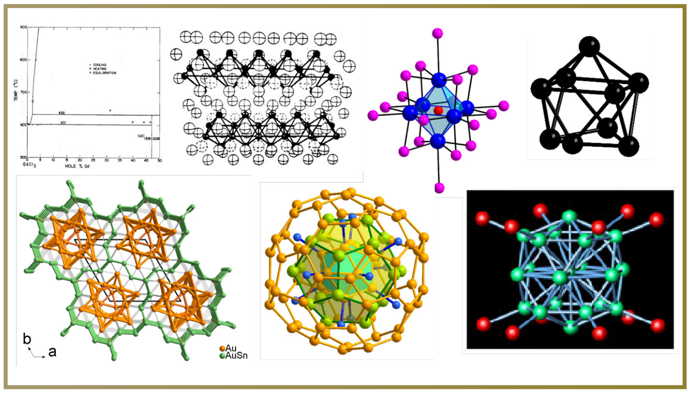

Figure 2 A few highlights of the many accomplishments of John D. Corbett's research, 1953-2013, clockwise from upper left: The phase diagram of the $GdCl_3$/Gd system and part of the crystal structure of Gd_2Cl_3; an isolated, interstitially stabilized transition metal cluster anion, $[\{ZM_6\}X_{18}]^{n-}$; the Zintl anion $\{M_9\}^{n-}$ as for example in $(2,2,2\text{-crypt-}K^+)_3\{Sn_9^-\}_3(en)_{1.5}$; an In-centered In_{20} fullerene cluster (green) with 12 bridging In atoms in $Na_{28}In_{56}$; a Au_{12} center in the multiply endohedral shells of clusters in the stuffed 1/1 Bergman-type approximant to the $Na_{13}Au_{12}Ga_{15}$ quasicrystal; gold stars in the polyanionic network of $Ca_{14}Au_{46}Sn_5$.

time, it took a while to determine the crystal structure, and it showed, as in the figure, octahedral gadolinium clusters connected via trans edges to chains surrounded by chloride "ligands," unbelievable in 1973![5]

Octahedral clusters were subsequently found in many of the rare-earth metals, with Sc, Y, and Gd as the main players, and others being sesquihalides, R_2X_3, and the spectacular monohalides, such as YCl and GdCl. Unlike ZrCl, these clusters, as in $GdClH_{0.6}$, were later found to exist only with considerable amounts of impurities, including "ubiquitous" elements such as H, C, N, O, and were not easy to detect by X-ray diffraction with respect to their graphite-like crystal morphology. Thus, a fantastic, completely unanticipated chemistry emerged in which not only the mentioned light atoms but also a huge variety of transition-metal atoms acted as "interstitials" (endohedral atoms sequestered within the cluster). These are necessary because the rare-earth atoms have only three valence electrons; note that in molybdenum clusters such as in $Cs_2[\{Mo_6\}Cl_{14}]$ there are twenty-four electrons available for bonding in the $\{Mo_6\}$ cluster and in $K_4[\{Nb_6\}Cl_{18}]$ 16 for the $\{Nb_6\}$ cluster. Even in $\{Zr_6\}$ clusters, an endohedral atom is needed, such as the single carbon atom in $Cs[\{CZr_6\}I_{14}]$[6] shown in Figure 2. In this connection, the first "alloy clusters" were observed, compounds in which the light main-group atoms are substituted by transition metal atoms, as in $Cs[\{MnZr_6\}I_{14}]$.[7] Electron-rich cluster complexes were in most cases isolated in "condensation" through common halide ligands and/or through common vertices, edges, or even faces of the clusters. These discoveries opened a vast area of new research pioneered in Ames and complemented at a few other places. Next on Corbett's agenda were metal-rich tellurides, such as Sc_9Te_2, in 2000 the scandium-richest telluride.[8] All this chemistry afforded special techniques, reactions in sealed refractory metal ampules (niobium, tantalum) under strictly anaerobic conditions.[9]

John's first publication not related to his Ph.D., in 1955, was entitled "The Solubility of Some Metals in their Molten Halides."[10] The trajectory was set and led to solids with the lower oxidation states of many transition and post-transition metals, such as cadmium (Cd_2^{2+}), gallium ($Ga[AlCl_4]$), bismuth (Bi_9^{5+} or Bi_5^{3+}), selenium (Se_8^{2+}), and tellurium (Te_4^{2+}) and even mixed-halide cations (ICl_2^+), all stabilized with a Lewis acid, often $AlCl_3$, in solids such as $(Bi^+)(Bi_9^{5+})[HfCl_6]_3$.[11] Complementary to the frequent (homo)polyatomic cations are (homo)-polyatomic anions, such as Ge_9^{4-}, Sn_9^{3-}, Sn_9^{4-}, Sb_7^{3-}, Pb_5^{2-}, Sb_4^{2-}, Bi_4^{2-}, and, as a heterometallic example, $Sn_2Bi_2^{2-}$. These so-called Zintl anions exist either in solids with "active" metals as the cations or in solution. One of John's great achievements was to use ethylenediamine (en) at ambient temperature, with crown ethers or cryptands sequestering the alkali metal cations as in $[K^+(crypt)]_2Sn_4$, instead of liquid ammonia in which Zintl phases like NaTl are soluble.[12]

Consequently, these efforts led to even more complex and polar intermetallics and finally to quasicrystals and their approximants. Electron-deficient clusters of indium and thallium, such as In_{11}^{7-}, Tl_7^{7-}, Tl_9^{2-}, Tl_{13}^{11-}, or even $In_{10}Zn^{8-}$ and $Tl_{11}Pd^{7-}$, as well as multiply endohedral fullerene examples, turned out to be relatively common. In the solid state, these clusters can form complicated networks, as in $KSrIn_7$ or Ba_2AuTl_7. Structural characterization of numerous crystalline approximants containing icosahedra and dodecahedra, for example in the cubic $ScZn_6$, Mg_2Zn_{11}, and $Mg_2Cu_6Ge_5$, showed that particular doping strategies could reach a calculated pseudogap in the electronic density of states, which has become a valuable synthetic tool for new icosahedral approximants and quasicrystals. John went into this area of research with a boyish joy to explore and to discover the unimaginable, stating, "It is the wonder and excitement of finding the unprecedented and unimaginable that makes research enjoyable, even exhilarating, and worthwhile."

And then there was his fascination with gold partial structures in complex polar intermetallics such as in $Ca_{14}Au_{46}Sn_5$.[13] Gold-rich polar intermetallics exhibit unprecedented and fascinating structures ranging from infinite one-dimensional tunnel structures, through two-dimensional wavy Au sheets, to aggregates of Au_4 tetrahedra and numerous three-dimensional extended structures.

John was a world-renowned leader in all these diverse areas thanks to his never-ending curiosity and a never ebbing "supply" of graduate students, postdoctoral associates, visiting scholars, and guest professors. It was always fun to work with him even though expectations were high, and he could be impatient at times. On his desk there was a sign saying "Lord, grant me patience, but hurry!" And he included this quote in his e-mail signature. He was his own harshest critic. His paramount focus on scientific work was legendary, even more so after his wife, Irene, passed away in 1996.

AWARDS AND HONORS

John won numerous awards for his significant accomplishments, including the ACS Award in Inorganic Chemistry from the American Chemical Society (ACS), a Humboldt Research Award in 1986, the John C. Bailar Jr. Medal from the University of Illinois in 1988, the ACS Award for Distinguished Service in the Advancement of Inorganic Chemistry in 2000, the Frank H. Spedding Award for Outstanding Contributions to Science and Technology of the Rare Earths in 2005, the Terrae Rarae Prize in 2007, and the ACS F. Albert Cotton Award in Synthetic Inorganic Chemistry in 2008. His sixty-year service at the Ames Laboratory was recognized by the DOE with awards for Outstanding (Sustained Outstanding) Scientific Accomplishments in Materials Chemistry in 1987 and 1995. In 2001, he was named an honorary professor by the Fujian Institute of Research on the Structure of Matter in Fujian, China.

The scientific community recognized and honored his achievements through a number of dedicated journal and book issues, starting with a special issue[14] of the *Journal of Less-Common Metals* on the occasion of his sixtieth birthday in 1986, followed by a special issue[15] of *Zeitschrift für Anorganische und Allgemeine Chemie [Journal of Inorganic and General Chemistry]* on the occasion of his seventieth birthday in 1996. For his eightieth birthday, twenty-two former Ph.D. and postdoctoral students contributed chapters to the book *Inorganic Chemistry In Focus III*[16] in 2006, and his eighty-fifth birthday was recognized by a special issue[17] entitled "Polar Intermetallics, Clusters and Cluster Complexes," of the *European Journal of Inorganic Chemistry* in 2011, supplemented by a "viewpoint" of J. D. Corbett entitled "Intermetallic Studies and Bonding Concepts." Finally, the community honored John with a memorial issue of *Inorganic Chemistry* entitled "John D. Corbett (1926–2013): 60 Years of Metal-Rich Chemistry" in 2015.[18]

FINAL THOUGHTS

Those who knew John D. Corbett personally—family of course, friends, colleagues, and students—will remember the slender, tall man with a shock of wavy white hair who, almost until his last day(s), did frontier research in inorganic and materials chemistry seven days a week, with a passion that became even more essential to him after Irene passed in 1996, at the age of seventy. John refused to sell the spacious family home, standing up for his independence. Sunday afternoon was the time to prepare meals for the following week, with the aid of a cookbook his communications-professor daughter Julia had written, *Solstice Soup–Sumptuous Winter Soups from Around the World*. For example, he enjoyed making Lola's Nine-Bean Soup, a recipe he had slightly modified, as his handwriting in the booklet attests.


Figure 3 John D. Corbett fishing at Snake River near Jackson Hole, Wyoming, 2007. *Courtesy of Julia B. Corbett.*

John's grandfather, John Henry Corbett manufactured bricks from the gray-brown soil of eastern Washington. His father-in-law, Oscar Lienkaemper, worked in an orchard during the Great Depression in a little town on that same dry side of the state. In his youth in the Yakima valley of eastern Washington, John had a pet saw-whet owl in addition to his trained prairie falcons. He also was a lifelong angler as shown in the 2007 photo of John at Snake River near Jackson Hole, Wyoming, during one of his short but yearly visits to his daughter Julia's cabin, a couple of rivers away.

It's appropriate that a man who truly loved his work, and who at age eighty-seven went to his office almost daily, would pass away on Labor Day, September 2, 2013, six days after he suffered a severe stroke. Until then, as a complement to all his brain work, he treasured physical labor in his elaborate garden, growing fruits and vegetables. John loved classical music and lingered after church to hear the organ recessional. He adored great food and enthusiastically explored ethnic cuisine during his world travels to chemistry conferences. His last passport had only a few unstamped pages. After travels, John was always glad to return to the lab, and glad to write original research papers where he could understand what he was doing during the process of writing. "Back to work" was an important phrase he used to end idle talk or gossip or a joint lunch.

ACKNOWLEDGMENTS

This memoir is based in part on the obituary by myself, Anja-Verena Mudring, and Kenneth R. Poeppelmeier published in 2013 in *Angewandte Chemie [Applied Chemistry] International Edition,*[19] the 2015 editorial by Gordon J. Miller, myself, and Anja-Verena Mudring in the special Corbett issue of *Inorganic Chemistry,*[20] as well as an entry on Corbett by Kathy Svec in the *Iowa State University Biographical Dictionary*.[21] Additional obituaries were published in 2013 by Ashok K. Ganguli in *Current Science*[22] and in 2014 by Susan M. Kauzlarich in *Comments in Inorganic Chemistry*.[23] Insights into John D. Corbett's personality can also be found in the book *Seven Summers: A Naturalist Homesteads in the Modern West,* authored by his daughter, Julia B. Corbett, in 2013.[24]

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