Inorganic Chemistry
Editorial
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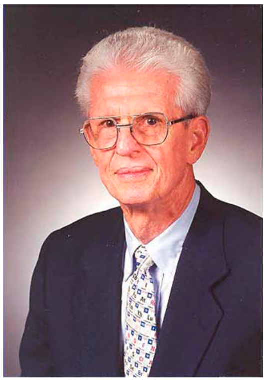
Corbett Special Issue Editorial

John Dudley Corbett was born March 23, 1926, in Yakima, WA. He was a 1944 graduate of Yakima High School and completed his undergraduate studies, subject to wartime conditions, at three institutions: North Dakota Teachers College; University of Wisconsin at Madison, where he learned general and chemical engineering; and ultimately the University of Washington in Seattle, WA, where he received a Bachelor's degree in 1948. He earned a Ph.D. in Physical Chemistry from the University of Washington with a dissertation on "Anhydrous Aluminum Halides and Mixed Halide Intermediates" under the guidance of Prof. Norman W. Gregory, who specialized in experimental investigations of the physical and chemical properties of metal halides.



Photograph from Ames Laboratory, US-DOE

John joined the Chemistry faculty at Iowa State University as well as the scientific staff of Ames Laboratory in 1952. In 1963, he was promoted to Professor of Chemistry and Senior Chemist of Ames Laboratory, serving as Department Chair from 1968 to 1973. He was Program Director of Materials Chemistry from 1974 to 1978, and in 1983 he received Iowa State University's highest honor for faculty by being named a Distinguished Professor. During his academic career, John mentored 41 Ph.D. students, 15 M.S. students, and 71 postdoctoral scientists. He published over 450 articles in peer-reviewed journals (more than 220 in *Inorganic Chemistry*!) and presented over 330 invited seminars around the world. He managed an active and vigorous research program throughout his career and was mentoring three postdoctoral students in research activities supported by the U.S. National Science Foundation and U.S. Department of Energy (DOE) when he passed away on September 2, 2013.

Throughout his scientific career, John and his group explored new vistas of inorganic compounds and followed up pioneering accomplishments in synthesis with thorough structural characterizations, physical property measurements, and analyses of electronic structure. His work had tremendous impact and broadened our understanding of chemical bonding in complex inorganic solids. On the basis of his scientific accomplishments, he received numerous awards including the ACS Awards for Inorganic Chemistry in 1986 and for Distinguished Service in the Advancement of Inorganic Chemistry in 2000 and the F. Albert Cotton Award in Synthetic Inorganic Chemistry in 2008, the DOE awards for Outstanding Scientific Accomplishments in Materials Chemistry in 1987 and for Sustained Outstanding Accomplishments in Materials Chemistry in 1995, as well as the 11th Frank H. Spedding Award in 2005. He was elected as a member of the U.S. National Academy of Sciences in 1992.

John's scientific career included many major areas of accomplishment that originated with imaginative synthetic principles or procedures and often revealed unprecedented or inconceivable species, many of which have been included in chemistry textbooks:

1. Molten Salts and Acid Stabilization. In his early work, John recognized that significant solubilities of certain metals in their molten halides were evidence for the existence of these metals in lower oxidation states. Gaseous metal−metal halide systems for Zn, Cd, Sb, and Bi substantiated this. He was the first to recognize that a Lewis acid such as $AlCl_3$ would favor the stability of reduced states of metals, which led to the first isolation of $AlCl_4^-$ salts of Cd^I, Ga^I, Bi_5^{3+}, Bi_8^{2+}, Se_8^{2+}, Te_4^{2+}, and I_5^+ species. John also recognized that a eutectic in the Bi−$BiCl_3$ system required the existence of a new solid, which led to structural identification of the unique Bi_9^{5+} cage in Bi_6Cl_7. Several additional solution studies confirmed these and other species.

2. Zintl Polyanions and Related Zintl Phases. John established firm evidence for molecular polyanions via solutions of alkali-metal alloys in molten halides, e.g., for Bi^{3-}, Sb_3^{3-}, etc. His major discovery was that cryptand complexation of alkali-metal cations destabilized the competing intermetallic phases. He subsequently obtained the first isolation and structural characterization of many stable polyanions from ethylenediamine, e.g., Sb_7^{3-}, Sb_4^{2-}, Pb_5^{2-}, Sn_9^{4-}, Sn_9^{3-}, $Sn_2Bi_2^{2-}$, Ge_9^{4-}, and Bi_4^{2-}, and further identified closely related clusters in intermetallic compounds, e.g., Hg_4^{8-} and Bi_4^{2-}. In recent years, he and his co-workers have unraveled new bonding motifs in unusual valence compounds, e.g., $Ca_{31}Sn_{20}$, $NaGaSn_2$, $Ca_{16}Sb_{11}$, $Ca_{6.2}Mg_{3.8}Sn_7$, $K_4AuTlSn_3$, $K_5As_3Pb_3$, etc. This effort includes incorporating heavier elements like Pt, Au, Tl, and Pb, which have demonstrated spectacular bonding characteristics associated with relativistic effects in these elements.

3. Reduced Metal Halides; Tantalum as a Container. Successful studies of a great many reduced metal halide, chalcogenide, and pnictide systems of group 1−4 metals as well as numerous intermetallics became possible following John's seminal development of tantalum and niobium as excellent reaction containers at elevated temperatures. These procedures are now utilized around the world for the preparation of air- and moisture-sensitive metal-rich reactions. Numerous new halides followed: (a) rare-earth dihalides; (b) metallic diiodides $M^{+3}(I^-)_2e^-$ for La, Ce, Pr, Gd, and Th; (c) unique extended clusters such as Gd_2Cl_3 and Sc_7Cl_{10}; (d) unique layered ZrCl, ZrBr, and HfCl and new halides, $ZrCl_2$, ZrI_3, HfI_3, etc. Extension of this halide chemistry to chalcogenides during the past 10 years has yielded many new compounds and extended metal−metal bonding motifs, which range from infinite columns (Sc_2Te and Sc_9Te_2) through puckered sheets (Sc_8Te_3 and $Lu_{11}Te_4$) to

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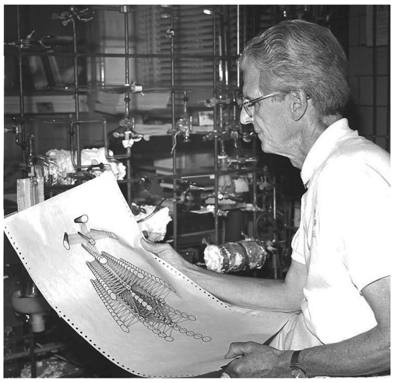
unprecedented substitution structures (Lu_7Te and Lu_8Te). Formal polymerization of Sc_2Te by metal-atom substitution yields Sc_6MTe_2 (M = Pd, Ag), and figurative conversion of the unusual Gd_3MnI_3 structure gives infinite metal sheet and rod constructions in $Sc_5Ni_2Te_2$ and $Y_5Fe_2Te_2$, respectively.



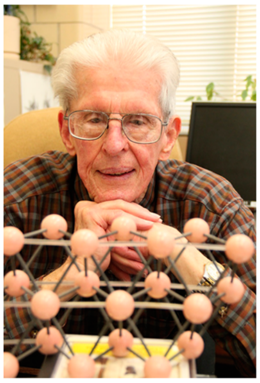
Photograph from Ames Laboratory, US-DOE

4. Impurity Troubles and Interstitially Stabilized Metal Clusters. The use of high temperatures for strongly reducing systems means particular thought and care are necessary to achieve high-quality products in high yields. John's studies revealed that many compounds involving alkali, alkaline-earth, and rare-earth metals are uniquely stabilized by hydrogen or other atomic impurities. An insidious family of Mn_5Si_3-type intermetallic phases exists, which were shown to be virtual sponges for impurities, formulated as A_5B_3Z phases, meaning that the structure type alone is an inadequate measure of the purity. Upon recognizing the significance of adventitious impurity atoms in these metal-rich compounds, John utilized this chemical phenomenon synthetically and led the discovery and development of a very large family of, for example, $R_6(Z)X_{12}$-type cluster halides of rare-earth metals or zirconium uniquely stabilized by interstitial atoms Z. In these interstitially stabilized cluster compounds, the species Z spans numerous nonmetals, semimetals, and transition metals, more than 30 elements overall. Variations of the interstitial atom Z as well as added countercations allowed the systematic development of numerous new structures. The first extraction of zirconium clusters into nonaqueous solvents with suitable ligands led to new derivatives.

5. Complex Intermetallics, Quasicrystals, and Their Approximants. In his later years, John directed his attention and imagination to complex intermetallic polyanions, networks, and quasicrystals. His efforts showed that electron-deficient clusters from group 13 (3) elements are relatively common, especially among the heavier elements, e.g., Tl_9^{2-}, In_{11}^{7-}, Tl_{13}^{11-}, Tl_7^{7-}, $In_{10}Zn^{8-}$, $Tl_{11}Pd^{7-}$, as well as multiply endohedral fullerene examples. In the solid state, these clusters can also form complicated networks, as in $Na_{30.5}Ga_{53.6}Ag_{6.4}$, $KSrIn_7$, Ba_2AuTl_7, and phases in which Li, Mg, or Zn substitute for In. An especially significant contribution from his laboratory was the development of a model for a type of icosahedral quasicrystal through structural characterization of numerous crystalline approximants containing related icosahedra and dodecahedra. John focused his cluster experience on cubic examples, e.g., $ScZn_6$, Mg_2Zn_{11}, and $Mg_2Cu_6Ge_5$, and 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.

The foregoing clearly establishes the tremendous breadth and novelty that John Corbett generated in a scientific lifetime that spanned more than 60 years of wider ranging and creative synthetic successes. Almost the entire periodic table of the elements was his playground. And, like a child playing gleefully in a sandbox, John brought his youthful enthusiasm and energy to the research activities in his group. This vitality for research and love of fundamental science was contagious and inspired both his students and his colleagues. He remained an active and lively scientific speaker at national and international meetings.

Of the 120-plus students that John mentored, many were introduced to solid-state chemistry as graduate students at Iowa State University. Some joined his group as postdoctoral scientists after completing Ph.D. degrees in organometallic or other molecular-based disciplines. He worked with students whose graduate background emphasized theoretical chemistry and directed their development in experimental areas. Most of these students have gone on to successful careers in materials or solid-state chemistry, spanning industrial, academic, and government sectors around the world. The future of solid-state chemistry is being shaped by his former students and co-workers. Through the training of these researchers and his unparalleled energy and enthusiasm, John has had a major impact on the development and advances in solid-state, inorganic, and materials chemistry and related fields worldwide. As a humble reward for his ample accomplishments and a thank you for his guidance and friendship, we, former students, postdocs, colleagues, and friends, dedicate the papers of this issue to the memory of the late John D. Corbett.



Photograph from Ames Laboratory, US-DOE

Gordon J. Miller
Department of Chemistry, Iowa State University
Ames Laboratory, U.S. Department of Energy
Gerd Meyer
Department of Chemistry, Iowa State University
Anja-Verena Mudring
Department of Materials Science and Engineering, Iowa State University
Critical Materials Institute, Ames Laboratory, U.S. Department of Energy

■ AUTHOR INFORMATION

Notes

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