

NATIONAL ACADEMY OF SCIENCES

JAMES LYNN HOARD

1905—1993

A Biographical Memoir by
ROBERT E. HUGHES

*Any opinions expressed in this memoir are those of the author(s)
and do not necessarily reflect the views of the
National Academy of Sciences.*

Biographical Memoir

COPYRIGHT 1998
NATIONAL ACADEMIES PRESS
WASHINGTON D.C.



J. S. Howard

JAMES LYNN HOARD

December 28, 1905 – April 10, 1993

BY ROBERT E. HUGHES

JAMES LYNN HOARD, or Lynn as he was known to his many friends and colleagues, was a central figure on the faculty of Cornell's chemistry department for thirty-five years before his retirement in 1971. In the ensuing years, he continued his distinguished career in structural crystallography, appearing daily at his office immersed in the painstaking scholarship characteristic of his entire career. In a half century of meticulous and thoughtful research he gained international recognition for seminal and classic work on the stereochemical principles underlying high-coordination discrete complexes; for founding the basis for the icosahedral crystal chemistry of elementary boron and binary borides; and, inter alia, for providing critical insights into the mechanism of the oxygenation of the heme in hemoglobin.

Hoard's father, Charles Ellsworth Hoard, from Monongalia County, West Virginia, was in his mid-twenties when he brought his young bride Bertha Terpening Hoard from Iowa to Republic County, Kansas, to raise a family. At the turn of the century, then six strong, they moved to a farm near Elk City in Beckham County in the Oklahoma Territory, where Lynn, the sixth of seven children was born. He was five

when the family moved to Seattle, Washington, where he spent his formative years.

As a youth, Lynn was quietly competitive, determined to excel in every undertaking whether it was studies, a game of badminton, or playing the piano. This became a hallmark of his life and career—a self-driven, indeed stubborn, determination to do his best in every enterprise.

Throughout his life, Lynn was blessed with a remarkable memory that impartially delivered long discourses on any subject that interested him—phytography, meteorology, geography, Indian nations, musical scores, or the finest details of chemical structure. In his later years he could remember the names of his school teachers and the grades they gave him, a few of which he still contested. His versatility led him to consider undertaking a career as a classical pianist, and he interrupted his undergraduate program for a year of musical studies. He finally made the decision to turn to science, but the piano remained an integral part of his life.

Although he authored some 115 papers, Lynn was not a facile writer. He combined faultless syntax with precision and economy of expression. Each paper became a labor of love, written and rewritten, paragraph by paragraph, sentence by sentence, clause by clause. He devoted the same attention to papers from other authors sent to him for review, sometimes spending days reforming ideas, recalculating, and giving freely of his own contributions. Editors, recognizing this, sent him more than his fair share to review. He applied the same stringent criteria to his teaching and would spend hours trying to improve the clarity of a single important concept.

Scientific discussions with Lynn followed the cadences of his writing. Striving to get to the bright, hard core of an idea he would alternate reflective pauses with converging

attempts to separate wheat and chaff. It was a phenomenon well recognized by all of his colleagues and students. I recall my first encounter with Lynn when, as a new graduate student, I paid a courtesy call at his office. Almost four hours later, I left, launched into a lifetime association with Lynn and his family.

In 1927 Hoard graduated from the University of Washington magna cum laude in chemical engineering. He was also awarded Phi Beta Kappa, the first chemical engineering student at the institution to be so honored. He continued at the University of Washington, earning a master's degree in chemistry in 1929. He then went on to graduate work at the California Institute of Technology, an institution rapidly rising as a major world center in science. It was there that he met and worked with Linus Pauling, forming a lifelong friendship. Reflecting on those early years with Hoard, Pauling wrote,

One memory I have of him, from several occasions, is the following. He would have learned about something surprising that had been discovered in the field of science, perhaps just told to him by me. He would stand for some minutes with a look on his face that suggested strongly to me his feeling of surprise and pleasure about the new discovery—his mouth held somewhat open and his eyes seeming to flash with pleasure.

After completing his Ph.D. with Pauling in 1932, Hoard became one of the early pioneers in the application of X-ray diffraction techniques to the determination of crystal and molecular structures. In those days, the challenge of truly arduous and lengthy calculations required both determination and structural insight of investigators in this field. In the midst of the Great Depression, Hoard brought his newly acquired skills to Stanford University where he served as an instructor for three years. After a brief term at Ohio State University, he joined Cornell in 1936.

Lynn Hoard loved Cornell and Ithaca and was ever reluc-

tant to travel, although he frequently did so in later years. He came to Ithaca with his bride, Florence Fahey Hoard of Seattle, and raised a family of three sons, David and the twins Thomas and Laurence. In the early years, although under constant pressure from Lynn's participation in the Manhattan Project and his intense dedication to research, they nevertheless completed a major family project. With a visionary architect, they helped design, manage, and participate in the construction of a unique home, which they were to share for forty-five years. Modeled along the lines of a Frank Lloyd Wright design, it has been an Ithaca landmark, graced by carefully planned and beautifully kept gardens. The family and the household revolved around Florence and she remained the invariant focal point of Lynn's entire life.

While working to establish a successful scientific career, raise a family, and put down roots in Ithaca, Lynn Hoard, in the early days of World War II undertook, as did so many young scientists at the time, to contribute to the national defense. He joined a group at Cornell, sponsored by the Office of Scientific Research and Development through the National Defense Research Committee. The project was concerned with the development of flashless propellants for large Navy guns; the Cornell role was to study the mechanism of the combustion process and to conduct the evaluation of nitrocellulose, plasticizers, and other ingredients. Within a year, the young crystallographer from Caltech was put in charge of the Cornell team among whose participants were listed such familiar names as F. W. Billmeyer, Jr., J. G. Kirkwood, Franklin A. Long, and Henry Taube. Working in parallel with the Explosives Research Laboratory at the Carnegie Institute of Technology, the project was considered very successful.

While this project required Hoard to accommodate to

fields of science outside of his immediate expertise, he characteristically persevered in the task from 1942 to 1945, and was cited for his successes. He also found other uses for his structural knowledge; from 1943 to 1944 he participated in a program with the Manhattan Project and, as was acknowledged decades later, solved some important problems on the structure of uranium compounds.

In the early 1920s Roscoe Dickinson at Caltech made significant contributions to verifying the square planar, octahedral, and tetrahedral structures of a variety of complexes. This led Hoard to consider extending such work into the realm of high coordination complexes. Using Pauling's univalent radii and hard sphere packing principles, he made a priori predictions of seven-coordinate geometries for heptafluoro complexes of tantalum and niobium, as well as for the eight-coordinate octacyanomolybdate ion. In a letter to Hoard, Pauling suggested that the latter structure was much too difficult an undertaking. This was followed by another letter congratulating him for his success.

In Hoard's own words:

As expected from a priori considerations, the anionic complexes were found to be seven- and eight-coordinate species. These analyses provided the first examples of discrete complexes in configurations that approximated closely to the geometries of the C_{2v} monocapped trigonal prism, the D_{4d} square antiprism, and—most notably—the D_{2d} dodecahedron having triangular faces, eight vertices, and eighteen edges. This dodecahedron emerged as the coordination polyhedron of the octacyanomolybdate (IV) ion.

These early successes, termed classic by some distinguished observers, presaged Hoard's lifelong interest in the structural chemistry of complexes, an interest he steadily advanced for the next four decades. Pauling was later to assert,

Professor Hoard's work on the determination of the structure of coordination complexes has been a great contribution to knowledge. It is my impression that he has more contributions in this field than anyone else; he

must surely be considered one of the world leaders in this field. His work on the determination of the structure of complexes in which metal atoms have liganacy seven or eight has been especially important.

Another distinguished inorganic chemist, Professor Earl L. Muetterties observed,

Professor Hoard's work in the structural chemistry of discrete coordination compounds comprises a touchstone for other investigators. His analyses, from the first report of a seven-coordinate complex through pioneering studies of eight-, nine-, and ten-coordinate complexes, have been marked by a singularly comprehensive view of the field. This is particularly evident in his enunciation of stereochemical principles governing eight-coordination, an invariably cited standard.

In addition to pursuing the studies that led to complete elucidation of the discrete eight-coordination stereochemistry he had discovered, Hoard also undertook an extended, systematic study of high liganacy complexes of ethylenediaminetetraacetic acid (EDTA). Muetterties acknowledged the importance of this program in writing,

Hoard's parallel interest in the structural properties of multidentate ligands has resulted in an extensive series of papers on coordination compounds of EDTA. These papers remain the outstanding source of carefully measured and critically evaluated structural data for EDTA complexes. A dramatic illustration of the value of the insights developed by Professor Hoard was his prediction and subsequent discovery of a seven-coordinate complex of iron(III), a complex which had been thought to be unrealizable by the scientific community.

Both the range and depth of Hoard's work on the stereochemistry of metal complexes were magnified by the almost unprecedented precision and detail with which the results were reported. No meaningful cross-comparison was overlooked. Over the years, in some seventy papers exploring the subject, he created and interrelated a dense body of knowledge that is still being mined by others. Impor-

tantly, he also deduced structural principles that interlaced this panorama.

Commenting on this, Professor William N. Lipscomb, Jr., noted that

Hoard's studies have become the important prototypes for both others and himself in the recent intensive interest in compounds of high coordination number. The work has influenced the areas of stereochemistry, rearrangements, transition states, and the theory of chemical bonding. The care with which his x-ray diffraction studies have been carried out has given them a high degree of permanence, and the cumulative effect has had a strong influence upon both the fundamental knowledge and the standards of research in inorganic chemistry.

Similarly, in another vein, Professor Henry Taube pointed out that

Hoard has done work of outstanding importance to the development of structural inorganic chemistry. Its importance is not restricted to the crystalline solid state, but many of the results are so basic and of such far reaching significance as to affect profoundly the whole fabric of inorganic chemistry, including inorganic solution chemistry . . . Anomalous coordination numbers are as important to solution chemistry as they are to solid state chemistry (perhaps even more important because they are of direct significance to mechanisms of substitution reactions) . . . The principles that govern the structure in the solids are being delineated by Hoard—his 'instinct' in predicting unusual arrangements in the solid is, as far as I can tell, unerring—and these principles will apply also to structures in solution although, of course, with some modification.

It was characteristic of Lynn Hoard's approach to science that he did not—indeed, by nature, could not—turn away from difficult or seemingly intractable problems. His determination and self-confidence led him to pursue them relentlessly even if it took a decade of effort. Thus, quite independently of his ongoing programs on complexes, he chose to investigate the crystal chemistry of the element boron.

In the late 1940s and through the 1950s most crystallographic studies focused on structures with at least one moderately heavy element that would provide a reference point for determining the scattering phases and ultimately the structure. Molecular structures were largely confined to small molecules of known chemical structure. These constraints were driven by the primitive calculators available, the daunting computations required, and the absence of modern statistical analyses known as direct methods. It was in this context that he decided to undertake the structure determination of a crystal with fifty very light boron atoms per unit cell with unknown stereochemistry. It was my good fortune to join his group at this time and to share this adventure with him.

Lynn had earlier completed the landmark structure of boron carbide in which there appeared, for the first time, a structural element of twelve boron atoms at the vertices of a regular icosahedron. When we completed the structure of alpha-tetragonal boron, the icosahedron was established as the basic building block in the extraordinarily diverse array of boron polymorphs and higher borides. On seeing the results, Pauling wrote to say that it was one of the most beautiful structures he had seen.

Later work culminated in the structure of beta-rhombohedral boron, which is the thermodynamically stable polymorph of the element. More than a decade of effort in this field was brought together in 1965 in an authoritative treatise on the crystal chemistry of boron and higher borides that stands today as a primary reference in the field. Muetterties, the editor of the volume in which it appeared, later wrote:

When I first received Professor Hoard's chapter, which was written in collaboration with Professor Hughes, I was struck by the extraordinary attention to detail and by the precision given to the description of the very

complex solid phases associated with elemental boron and some of the other borides. This book has been reviewed in about ten different journals and magazines and, without exception, this chapter by Hoard and Hughes has been singled out as a major and outstanding feature of the book.

Professor Lipscomb in commenting on Hoard's studies on "compounds involving the important icosahedral B_{12} unit in boron itself and in borides" further stated that:

His most sustained, and most penetrating studies of complex systems have been the studies of beta-rhombohedral boron and tetragonal boron. From these studies he has developed, in collaboration with R. E. Hughes, a general set of principles for icosahedral units in boron and the very large number of borides having high boron content.

It is clear that Lynn Hoard, from his earliest works, earned the respect and ultimately the admiration of distinguished scientists in many fields. While to many this might be somewhat gratifying, as all of his colleagues would attest, it was totally irrelevant to Lynn's approach to or conduct of science. He answered to an inner judge. Nowhere was this more evident than in his choice of research areas.

Well past mid-career he began a new program on the stereochemistry of porphyrin derivatives. His objective was to examine model systems that might shed light on the mechanism of hemoprotein function. This was a major venture into an important and very active biological field—his first. It occupied his attention for the rest of his career.

Hoard reported his first structure of a porphyrin derivative in 1963, the year when there first appeared meaningful determinations of crystal structures and molecular stereochemistry for porphyrins. The principal obstacle to progress in this field was the great difficulty in producing single crystals suitable for X-ray diffraction analyses, especially for materials of biological importance. Crystalline disorder often precluded obtaining meaningful data; in most cases that

were tractable, heroic effort was required to account for the effects of disorder.

By 1965 Hoard had fully immersed himself in the field and characteristically had produced some of the highest resolution structures of iron-porphyrin derivatives. Combining his own results with a critical assessment of the available literature, he formulated a hypothesis about the effect of the spin state of iron on the stereochemistry of its interactions with the porphine skeleton, a proposal that was to be central to the understanding of the mechanism of oxygen binding in hemoglobin.

Each of the four possible combinations of ferrous (FeII) or ferric (FeIII) iron in a high- or low-spin ground state is realized in one or more of the hemes as these occur in the several families of the hemoproteins. From the low resolution maps of the hemoglobin structure available at that time it was assumed that the iron atom was centered in the plane of a rigid protoheme, bonded to the four nitrogen atoms in the framework, and directly attached to the globin framework through an axial complexing bond from the iron atom to an imidazole nitrogen atom of the proximal histidine residue. Molecular oxygen occupies the sixth position in the coordination group of the iron atom in the low spin oxyhemoglobin (oxy-H_b) molecule; there is, of course, no sixth ligand in the high-spin deoxyhemoglobin (deoxy-H_b) species.

Hoard, relying heavily on his deep understanding of the stereochemical principles governing metal complexes, firmly postulated that "the porphine moiety, as compared with an aromatic hydrocarbon of the benzene series, is quite susceptible to significant folding, ruffling, or doming when subjected to moderate stressing." He further asserted that "a substantial displacement ($\geq 0.40\text{\AA}$) of the iron atom from the plane of the four nitrogens to which it is bonded is a

normal structural property of all high-spin iron porphyrins.”

These two postulates formed the basis for a new understanding of the trigger mechanism that precipitated the allosteric transition accompanying the oxygenation and deoxygenation of hemoglobin. Max Perutz at Cambridge remarking that “Hoard predicted it all,” used these concepts to develop a detailed model of the transition that starts with the movement of the iron atom pressuring the histidine ligand and generating a cooperative shift of the two halves of hemoglobin through an angle of 15 degrees.

Hoard later commented that “Perutz has made full and generally perceptive use of our precise stereochemical data and our interpretations thereof for the iron porphyrins . . . He has put forward a boldly conceived and rather detailed structural model for the overall mechanism of oxygenation in which the conformational change attending the oxygenation of a single heme suffices to initiate cooperative interactions in the hemoglobin molecule.”

Professor Paul B. Sigler, reviewing the history of these developments observed:

The cooperative binding and release of oxygen by hemoglobin is critical to its function as a carrier of oxygen from the lungs to the tissues. The challenge to explain this remarkable phenomenon in stereochemical terms motivated Perutz and Kendrew to begin their now legendary crystallographic studies. Hoard’s seminal contribution to our understanding the triggering stereochemical event; i.e., the displacements of the heme iron from the plane of the porphyrin, illustrates an important principle in the field of structural studies; namely, that achieving high resolution and visualizing the stereochemical details is not just an exercise in crystallographic virtuosity but rather, the “details” of a high resolution image often provide a paradigm-shifting observation that is the key to a chemical mechanism. There is a natural tendency for all chemists and biologists to fill in the missing details of a low-resolution structure with their preconceived chemical bias; but more often than not they are wrong. Visualizing the event clearly

with precise data, even from carefully chosen model systems, provides the unexpected clue that moves the field forward.

Lynn continued his exacting work on porphyrin structures for another decade and, in addition to being called on to address national and international conferences, he contributed two dozen finely wrought papers to the field.

As the years went by, the Hoard household was never without visiting children and grandchildren. Larry and Patti would arrive periodically with daughter Laura; Tom and Deborah lived nearby, so young Sarah and Cameron were daily itinerants, while David and Donna's Elisa and Daniel in California were more likely to be summer visitors. And always, the Hoards were gracious hosts, welcoming visits, long and short, from former students, postdoctorals, and visiting dignitaries from home and abroad.

At a celebration of his sixty-fifth birthday I tried to express the warmth and wonder with which he was viewed with the following words:

After twenty years of close association with Lynn, I know better than to cite anecdotes that I will have to explain away for the next twenty years. After all, anecdotes tend to have an apocryphal flavor that does not stand up very well against the knitted brows of total recall. However, I am pleased to report that nothing has really changed in Ithaca. Interrupted conversations are still resumed in mid-sentence days later and the ebb and flow of ideas surges out into the hallways, across the laboratory and back into the office again. Each day, on into the evening, the creative process is renewed in an eternal struggle with syntax as sentences and paragraphs are forged, hammered and tempered until they pivot with delicate precision on the final semicolon. In recent years, Lynn has adjusted the tempo of his life to respond to increasing demands for his presence as a lecturer in such places as Rome, Cambridge, Zurich, Austria and Australia; such journeys are frequent now and his friends have sensed a growing wanderlust that was hitherto unsuspected. Nevertheless, even as he strides into Baker Lab freshly tanned from the Foro Romano, Lynn Hoard remains one of Ithaca's most familiar and important institutions.

James Lynn Hoard's scientific contributions were widely recognized throughout his career. In 1946 he was awarded a Guggenheim fellowship, which he pursued at the California Institute of Technology. He received a second Guggenheim award in 1960, which he used to consolidate his thinking about ongoing and future programs. He then received a very rarely awarded third fellowship in 1966. He traveled to Cambridge, England, and focused on the relationships between metalloporphyrin structures and biological mechanisms in hemoglobin.

In recognition of his great body of work in three important areas of structural chemistry, he was elected to the National Academy of Sciences in 1972. In 1977 the American Chemical Society presented him with the Award for Distinguished Service in the Advancement of Inorganic Chemistry.

Perhaps the most significant recognition he received was the warm esteem in which he was held by his Cornell colleagues, students, and friends for more than half a century.

SELECTED BIBLIOGRAPHY

1939

With H. H. Nordsieck. The structure of potassium molybdocyanide. The configuration of the molybdenum octacyanide group. *J. Am. Chem. Soc.* 61:2853-63.

1943

With H. K. Clark. The crystal structure of boron carbide. *J. Am. Chem. Soc.* 65:2115-19.

1951

With S. Geller and R. E. Hughes. On the structure of elementary boron. *J. Am. Chem. Soc.* 73:1892.

1954

With W. J. Martin, M. E. Smith, and J. F. Whitney. Structures of complex fluorides. The structure of sodium octafluotantalate, Na_3TaF_8 . *J. Am. Chem. Soc.* 76:3820-23.

1958

With R. E. Hughes and D. E. Sands. The structure of tetragonal boron. *J. Am. Chem. Soc.* 80:4507-15.

With J. D. Stroupe. The structure of crystalline uranium hexafluoride. In *Chemistry of Uranium, Collected Papers*. ed. J. J. Katz and E. Rabinowitch, pp.325-49. Oak Ridge: U.S. Atomic Energy Commission, Technical Information Service Extension.

1959

With H. A. Weakliem. The structures of ammonium and rubidium ethylenediaminetetraacetatocobaltate(III). *J. Am. Chem. Soc.* 81:549-61.

1961

With G. S. Smith and M. Lind. On the stereochemistry of ethylenediaminetetraacetato complexes of the iron group and related cations. In *Advances in the Chemistry of the Coordination Compounds*, ed. pp. 296-302. New York: Macmillan.

1963

With R. E. Hughes, C. H. L. Kennard, D. B. Sullenger, H. A. Weakliem, and D. E. Sands. The structure of β -rhombohedral boron. *J. Am. Chem. Soc.* 85:361.

With J. V. Silverton. Stereochemistry of discrete eight-coordination. I. Basic analysis. *Inorg. Chem.* 2:235-43.

With M. J. Hamor and T. A. Hamor. Configuration of the porphine skeleton in unconstrained porphyrin molecules. *J. Am. Chem. Soc.* 85:2334.

1965

With M. D. Lind and B. Lee. Structure and bonding in a ten-coordinate lanthanum(III) chelate of ethylenediaminetetraacetic acid. *J. Am. Chem. Soc.* 87:1611-12.

With M. J. Hamor, T. A. Hamor, and W. S. Caughey. The crystal structure and molecular stereochemistry of methoxyiron(III) mesoporphyrin-IX dimethyl ester. *J. Am. Chem. Soc.* 87:2312-19.

1966

With G. H. Cohen. The structure of the seven-coordinate trans-1,2-diaminocyclohexane-N, N' - tetraacetatoaquoferrate(III) ion in crystals of the calcium salt. *J. Am. Chem. Soc.* 88:3228-34.

1967

With R. E. Hughes. Elemental boron and compounds of high boron content: Structure, properties, and polymorphism. In *The Chemistry of Boron and Its Compounds*, ed. E. L. Muetterties, pp. 25-154. New York: Wiley and Sons.

1968

Some aspects of heme stereochemistry. In *Structural Chemistry and Molecular Biology*, eds., A. Rich and N. Davidson, pp. 573-94. San Francisco: W. H. Freeman.

With T. A. Hamor and M. D. Glick. Stereochemistry of discrete eight-coordination. V. The octacyanomolybdate(IV) ion. *J. Am. Chem. Soc.* 90:3177-84.

1969

With R. Countryman and D. M. Collins. Stereochemistry of the low-spin iron porphyrin, bis(imidazole) α,β,ν,δ -tetraphenylporphinatoiron(III) chloride. *J. Am. Chem. Soc.* 91:5166-67.

1970

With D. B. Sullenger, C. H. L. Kennard, and R. E. Hughes. The structure analysis of β -rhombohedral boron. *J. Solid State Chem.* 1:268-77.

1971

Stereochemistry of hemes and other metalloporphyrins. *Science* 174:1295-1302.

1972

With D. M. Collins and W. R. Scheidt. The crystal structure and molecular stereochemistry of α,β,ν,δ -tetraphenylporphinatodichlorotin(IV). *J. Am. Chem. Soc.* 94:6689-96.

1973

With J. J. Stezowski and R. Countryman. Structure of the ethylenediaminetetraacetatoaquomagnesate(II) ion in a crystalline sodium salt. comparative stereochemistry of the seven-coordinate chelates of magnesium(II), manganese(II), and iron(III). *Inorg. Chem.* 12:1749-54.

With W. R. Scheidt. Stereochemical trigger for initiating cooperative interaction of the subunits during the oxygenation of cobalthemoglobin. *Proc. Natl. Acad. Sci. U. S. A.* 70:3919-22.

Some aspects of metalloporphyrin stereochemistry. *Ann. N. Y. Acad. Sci.* 206:18-31.

1975

Stereochemistry of porphyrins and metalloporphyrins. In *Porphyrins and Metalloporphyrins*, ed. K. M. Smith, pp. 317-80. Amsterdam: Elsevier.