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John C. Bailar, Jr. (1904–1991): Father of coordination chemistry in the United States*

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John Christian Bailar, Jr., Professor Emeritus of Inorganic Chemistry at the University of Illinois and the universally acknowledged father of coordination chemistry in the United States, died on October 17, 1991 in Urbana, Illinois at the age of eighty-seven [1]. In the words of Theodore L. Brown, Director of the Beckman Institute at the University of Illinois, John "had an extremely important influence on the development of coordination chemistry in the United States. He, more than any other single person, was responsible for the advancement of coordination chemistry in this country" [2].

John symbolized all that is best in a university professor. A tall (6 ft. 3 in.), imposing figure, he was a kind man with a charming sense of humor and an engaging laugh; he knew a million stories and told them all very well. He was a devout Presbyterian (he served as a church elder) and politically conservative, although contrary to the usual trend he became distinctly more liberal in his later years. Despite his strong views, he was never judgmental and believed in letting people live their own lives and make their own decisions. He was open with others and generous with his time and energies. John was truly respected and admired and was a valued friend, colleague, scientist, and teacher. We are grateful for this opportunity to summarize his life and career [3–8].

EARLY LIFE

John Christian Bailar, Jr. was born in Golden, Colorado on May 27, 1904 in a small house on East Street, which in those days was at the edge of town. His

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Dedicated to the memory of Professor John C. Bailar, Jr.

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parents, John Christian Bailar and Rachel Ella Bailar (née Work) had been married in 1897 and from 1898 to 1901 both attended the University of Colorado, where John's father studied under the chemist Charles S. Palmer (1858–1939). The Bailars were the first married couple to enroll at and graduate from the university. Two years after his graduation, John's father was appointed an instructor in chemistry at the Colorado School of Mines at Golden; at the turn of the century, the school offered only one degree, in Mining Engineering, but a course in chemistry was part of the curriculum. The Bailars stayed in Golden for the next 15 years and while there had three children: two daughters and one son, John, Jr. John's father was a world-class gadfly and raconteur, who put his son, himself no mean teller of tales, in the shade. The father exerted a great influence on his son, and John, Jr. once said that his father "had the ability to explain things in terms that nearly everyone could understand, as well as the personal qualities that every good teacher must have — a love of students and patience with them, a real interest in and mastery of his subject, and a consuming desire to pass his knowledge on to others." No better assessment of the son's approach to teaching and his impact on students could be written.

John, Jr.'s chemical education began at an early age. When he was four or five years old, his parents built a house next door to the one in which they had been living. One morning, when the hod carrier was slaking lime to make mortar, John's father put a raw egg in the mortar box. When the egg was fished out a few minutes later, it was hard boiled from the heat of the reaction [9]. John is said to have eaten the egg and thereby learned his first lesson in thermodynamics.

John frequently accompanied his father to his combination office–laboratory, where he was allowed to help in simple laboratory operations such as folding filter papers and pouring liquids into funnels. During these visits and in conversations with his father, John acquired a good deal of chemical knowledge. Once, when he was about six years old, he asked his father why the bottle of hydrogen peroxide was labeled "H_2O_2" rather than simply "HO". John received an adequate explanation and learned about atoms, molecules, and formulas at an early age [5].

John began his formal education at the South Side School in Golden. The four rooms on the ground floor accommodated the eight elementary grades (two grades in each room), while the five rooms on the upper floor were reserved for the high school and principal's office, a typical arrangement for a small town at that time. In the entire city there were no telephones. John recalled that the owner of one of the few automobiles in town (limited in speed to five or six miles per hour) once generously offered to take him and his sister for a ride but that this expedition was ended unceremoniously after two or three blocks when a tire blew out.

John obtained his first job at about 13 years of age; he made shipping crates at the Coors Porcelain Company. He later worked on the construction gang enlarging the plant and finally was employed as a chemist analyzing clay. During summer vacations in his high school and college years, John also earned money for college

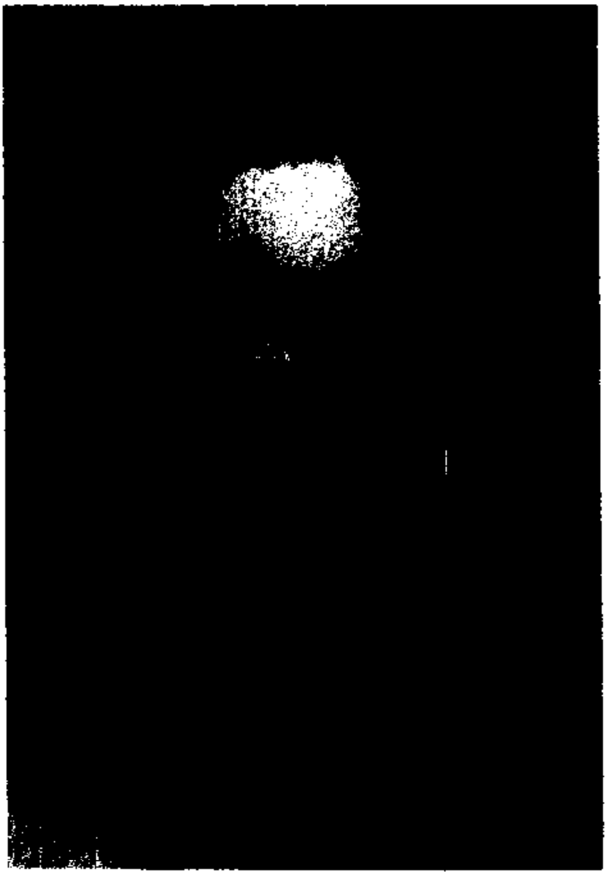

Fig. 1. John Bailar as a young student, ca. 1918.

expenses by working at the Coors "bottle house" where near beer (for Prohibition was still in effect) was bottled and packed into barrels for shipment.

UNDERGRADUATE EDUCATION

In 1921, at the age of 17, John enrolled at the University of Colorado in Boulder, about 30 miles from home. As a result of his early exposure to chemistry, he naturally took a course in freshman chemistry. He enjoyed and did so well in the class that the following fall at the beginning of his sophomore year he registered for the courses in qualitative analysis and organic chemistry, not realizing that this act was equivalent to declaring a major in chemistry, a most fortunate if unintentional decision.

The laboratory courses in chemistry made an indelible impression on John; the odor of hydrogen sulfide and other noxious gases was very strong because of

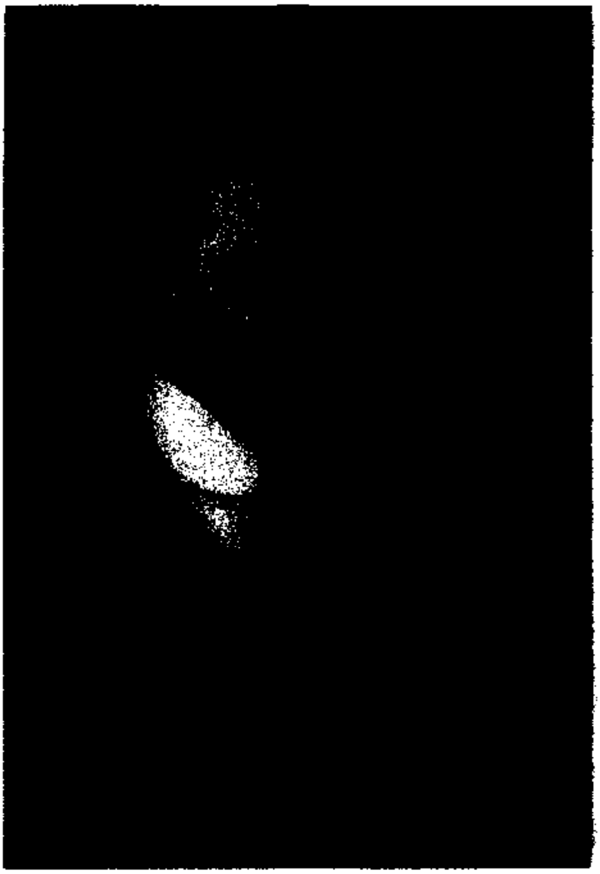

Fig. 2. High school graduation, 1921.

poor ventilation. In one experiment he followed the lab manual's instructions to put a little bromine into a test tube and drop into it a piece of white phosphorus "the size of a grain of wheat." A violent reaction ensued, shooting the flaming phosphorus out of the tube and onto the ceiling, where it continued to burn until it was all consumed. Much later John admitted that this was an experiment that he would not recommend for beginning students [5]. He even proudly showed the charred area to his older son, John III, who studied chemistry in the same laboratory and under the same point on the ceiling.

John received his B.A. magna cum laude from Colorado in the spring of 1924. During his senior year, he had been active in the local chapter of Alpha Chi Sigma, the professional chemistry fraternity, whose members elected him as delegate at the National Conclave to be held at Pittsburgh, PA that summer. John had an interest in learning more about the "east", and in the course of reading college catalogues discovered that the summer session at the University of Michigan would open only two days after the close of the Pittsburgh Conclave. He therefore decided to spend the summer session in Ann Arbor, living at the Alpha Chi Sigma house. Curiously, he registered at the University of Michigan as a graduate physics major, taking courses in electromagnetism, atomic structure, and X-ray diffraction; the latter was taught by Sir William Lawrence Bragg (1890–1971), who was visiting from England. John did not enjoy the courses, however, partly because he was not well prepared for them and because one course was taught by a visiting professor from Denmark whose English thoroughly mystified the young student.

John returned to the University of Colorado at the end of the summer of 1924 to enroll in the masters program in chemistry. He was awarded a one-year fellowship, and his research with the inorganic chemist Horace B. Van Valkenburgh (1883–1961) resulted in his M.A. thesis, "Nitrogen Tetrasulfide and Nitrogen Selenide: Preparation, Molecular Weight, and Some Properties" (1925). It describes improvements in the preparations of N_4S_4 and N_4Se_4 and the reactions of these substances with water and ammonia, and it formed the basis of his first published paper [B1]*.

GRADUATE STUDIES

During his summer stay at the University of Michigan in 1924, John had learned of the famous organic chemistry professor, Moses Gomberg (1866–1947) [B189,B223], and he thought that it would be a great privilege to work with him. Accordingly, John applied for a fellowship at Michigan. After receiving word that his application was successful, John wanted to make sure that he would be allowed to carry out his doctorate research with Gomberg, and so before accepting the appointment, he inquired about this. The response John received is a reminder of how things have changed since the 1920s: the Chemistry Department at Michigan informed John that, of course, *all* of the doctorate students in organic chemistry did their work with Professor Gomberg!

John returned to Ann Arbor in the fall of 1925 and immediately began his research. Gomberg was an adherent of the old European system and closely supervised his students, regarding them as little more than his "hands." He would come to the laboratory five or six times a day and ask his students, "What have you done since I saw you last?" Because the Professor had visited only two hours earlier, the correct answer to the question, which neither John nor the other students gave him, was "I have done what you told me to do." In later life, John deliberately did not follow Gomberg's example; instead he always gave his research students considerable freedom and the opportunity to do their own experiments and try their own wings [5].

One day Gomberg came into the laboratory when John was trying to get a brown, sticky syrup to crystallize. John had worked on it for some days without any promise of crystals at all. Gomberg took the dish in his hand and commented, "This

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* Reference citations prefixed by the letters "B", "P", or "R" refer to the articles, patents, or reviews, respectively, by John C. Bailar, Jr. in the Bibliography at the end of this article.

looks very promising." He added a few drops of benzene to the brown oil, rubbed it with a stirring rod, added a few drops of ligroin, rubbed some more with his stirring rod, and with his eye still fixed on the dish, suddenly, the entire mass crystallized. John asked, "How did you do that?" and received the grave reply, "One gains by experience." He always suspected that there was more than experience involved but was nevertheless impressed by Professor Gomberg's knack for knowing just what to do.

Gomberg is best known for his research on free radicals, especially the triphenylmethyl radical, and John's Ph.D. thesis research dealt with the synthesis of halogen-substituted tetraarylpinacols by the reduction of diarylketones with a mixture of magnesium and magnesium iodide. He investigated the possible dissociation of these pinacols to ketyl radicals in solution by constructing Beer's law plots and looking for non-ideal behavior. Several of the pinacols showed an increase in absorptivity upon dilution consistent with their dissociation to ketyls. He also studied the relative rearrangement rates of differently substituted pinacols to the corresponding pinacolones.

John spent three years at Michigan. At the beginning of his last semester, Gomberg came into the laboratory one day with a troubled look on his face and said "Mr. Bailar, we have just discovered that you have never taken a course in gas analysis. This course is required of everyone who is to get a Ph.D. degree." "But no one told me about this when I first came." "Yes, but nonetheless, you must take the course." John was upset, for, while ready to write his thesis, he was suddenly confronted with the necessity for taking another course. He spoke with the professor in charge of the gas analysis course, who asked him what work he had done with gases. John recalled some experiments that he had done in a physical chemistry course and his analyses of flue gases while working for the Coors Porcelain Company. The professor commented that these were significant experiences and that he would consider the course requirement satisfied if John would do one experiment that he would assign. The relieved student quickly agreed.

John once said that his days in Michigan were not always happy ones, and at times he had doubts that he would ever be a good chemist. He felt that his research did not go particularly well and that he did not make many friends. The professors and students at Michigan thought that there were only two good universities in the United States (Harvard and Michigan) and felt that John would not amount to much because he had come from the University of Colorado [5]. However, the granting of his Ph.D. in 1928 for his thesis "Studies in the Halogen Substituted Pinacols, and the Possible Formation of Ketyl radicals, R_2C–OMgI" represented a new beginning for him [B2,B3].

UNIVERSITY OF ILLINOIS

During his last two years at Michigan (1926–1928), John was a teaching assistant in general chemistry, and he enjoyed the job immensely. He decided that

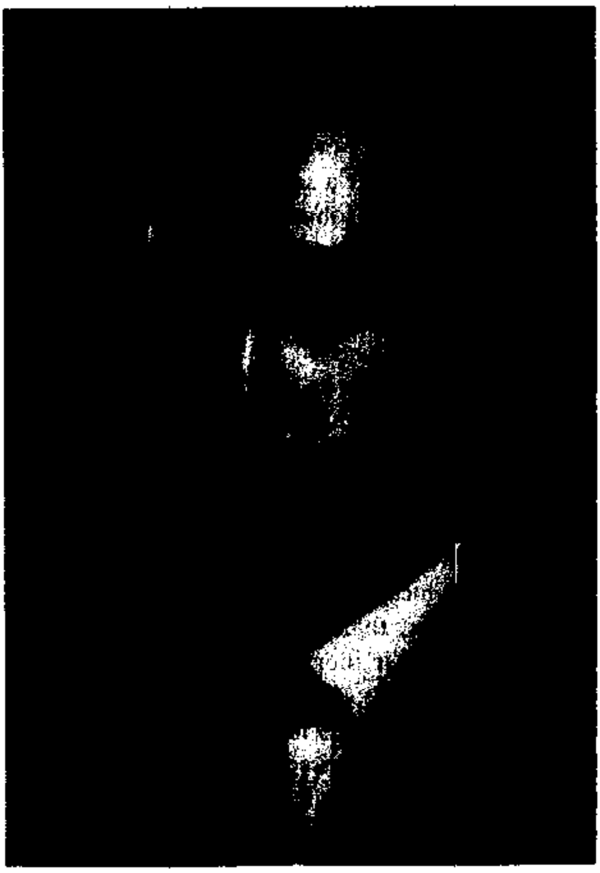

Fig. 3. John Bailar while in graduate school, October 1926.

he wanted to get a position teaching in a large university, preferably in a small town. Gomberg, however, thought that John should go into industrial work and arranged for interviews at the du Pont plant in Buffalo, NY and the Eastman Kodak Company in Rochester, NY. John shortly thereafter received an offer from Eastman asking for his decision by a certain date. Meanwhile, he had applied for teaching positions at the University of Illinois and another, less prestigious school. He had learned of the Illinois position from a letter that the inorganic chemist B Smith Hopkins (1873–1952) [B224] had written to Prof. Hobart H. Willard (1881–1974), who was in charge of analytical chemistry at Michigan. The young student showed the letter to Gomberg and told him that this was exactly the sort of position he desired. "No, Mr. Bailar," came the reply, "Illinois doesn't need any more organic chemists, for they already have a strong group, with Adams, Marvel, Fuson, and Shriner." Disheartened, John took the letter back to Willard, who asked if the job was of interest. John replied that it interested him greatly, but before John could say that Professor Gomberg saw no point in applying, Willard said "I'll get that job for you."

On the strength of Willard's word, John turned down the Eastman job before hearing from Illinois; not surprisingly, Gomberg was more than a little displeased with his headstrong student for taking this action. Fortunately, Willard's letter of recommendation resulted in an offer from Illinois, at a salary of $2100, $300 more than had been indicated in Hopkin's original letter. John immediately wrote to the Head of the Department of Chemistry at Illinois, Roger Adams (1889–1971), one of America's foremost organic chemists [10], accepting the job. Adams had made Illinois one of the great centers of organic chemistry in the United States; John was soon to make it a similar center for inorganic chemistry.

John joined the staff of the University of Illinois as an Instructor in 1928. His immediate supervisor was Prof. Hopkins, who was in charge of general and inorganic chemistry. Although John considered himself an organic chemist, Hopkins assigned him teaching duties in the freshman courses, which were then devoted almost entirely to descriptive inorganic chemistry. At the time, inorganic chemistry was a minor branch of chemistry in the US, and only a few universities offered graduate work in the field, the best known being MIT, Cornell, Chicago, Illinois, Ohio State, California, and Stanford. When John arrived at Illinois, more than a hundred graduate students were majoring in organic chemistry but only two in inorganic chemistry. Both were studying rare earth compounds with Prof. Hopkins, Asst. Prof. Harry C. Kremers (1889–1958), and Leonard F. Yntema (1892–1976). In 1926, two years before John's arrival, Hopkins and Yntema had announced their discovery of the long-sought element 61, which they named "illinium," a discovery that was never confirmed.

Interestingly, John was urged to join this small group, for it was thought that he could use his organic training to prepare organometallic derivatives of the rare earths and thereby separate these difficultly separable elements by distillation, a task later accomplished by means of gas chromatography by his former student Robert E. Sievers [11]. Although John did not accept this invitation, his research notebooks from October 1930 contain descriptions of attempts to react UBr_4 and UO_2Cl_2 with phenylmagnesium bromide. However, most of his early research projects centered on studies of alkyl- and alkoxy-substituted tetraarylpinacols along lines similar to those in his Ph.D. thesis [B6,B9], the rearrangement of azoxybenzene [B15], the Cannizzaro reaction [B18], and on experiments related to the qualitative inorganic analysis laboratory course that he taught [B5,B7]. Among the latter were unpublished attempts to prepare the then unknown perbromate ion.

The timing of John's arrival at Illinois was not particularly auspicious: the Depression began one year later, and the department was forced to dismiss a man who had been offered a job as an Instructor in 1929. In addition, it was then customary at Illinois (and other universities) to hire young Ph.D. chemists just out of graduate school to teach for two or three years and then to move them on to jobs elsewhere. John did not know of this policy at the time that he was hired, although he once said that he probably would have accepted the position anyway. During John's first few years at Urbana, Carl Shipp "Speed" Marvel (1894–1988) [12] sent him some senior research students and one graduate student, Theophilus Parsons, who worked with John for his Ph.D. degree [B15]. However, Marvel let it be known that John would get no more graduate students in organic chemistry. It thus seemed that John's career at Illinois was nearing an end; however, the tide of events was about to change.

THE SWITCH TO INORGANIC CHEMISTRY

Like a number of the most important late 19th-century coordination chemists such as Sophus Mads Jørgensen (1837–1914) [13], James Lewis Howe (1859–1955) [14], Lev Aleksandrovich Chugaev (1873–1922) [15], and even Alfred Werner himself (1866–1919) [16,B167,R46], John was trained as an organic chemist and entered inorganic chemistry through the back door, so to speak [17]. He had already become deeply interested in the subject of isomerism during his graduate studies in organic chemistry. One day, during his second or third year at Illinois, while teaching a class in freshman chemistry, John wrote on the blackboard one of the hydrolysis products of antimony trichloride, the oxychloride, SbOCl. A student raised his hand and said that he wanted to ask something about "that antimony hypochlorite." After explaining the student's error, it suddenly occurred to John that it might be possible to have inorganic isomers, and immediately after class he went to the library to look into the matter. He later said, "That minute I stopped being an organic chemist" [18]. During the next few months he tried to prepare pairs of isomers, such as thallous hypochlorite/thallic oxychloride and sodium sulfoselenate/sodium selenosulfate, but without success. Eventually he realized that the Tl^+ ion is too easily oxidized and the Se^{6+} ion too easily reduced to allow isolation of the necessary species.

During these experiments, John continued reading the inorganic literature in the hope of finding more examples of inorganic isomers that he might prepare. By the end of 1930, he had learned about coordination compounds and the many examples of different kinds of isomers that they exhibit. In his words, "Here I found a field that fascinated me and in which I saw many, many interesting research problems. My entire feeling toward the chemical profession changed. I had found my niche." His articles on inorganic isomerism [B7,B8] give an insight into his early thinking on the subject with which his name has become so closely identified. Not since Alfred Werner has there been so great an inorganic stereochemist as John Bailar was to become.

Because his very first venture into this area has achieved classic status, it is illuminating to learn of its genesis in John's own words:

"In 1893 Paul Walden [1863–1957] discovered the very interesting inversion reaction which bears his name [19] ... It was an extremely important discovery, for it called attention to the chemists of that day that reactions have mechanisms and, that in the examples which Walden furnished, there must be two different reaction mechanisms involved. During my reading of Werner's work on coordination compounds [20,21], I had read that he carried out the reaction *levo*-$[Coen_2Cl_2]Cl + K_2CO_3 \rightarrow$ *dextro*-$[Coen_2CO_3]Cl + 2KCl$. It occurred to me that, since Walden had converted *dextro*-chlorosuccinic acid to the hydroxy acid by treatment with potassium hydroxide and with silver oxide and had obtained an inversion of configuration in one of the cases, it might be possible that, if we repeated Werner's experiment, using silver carbonate instead of potassium carbonate, we might also get an inversion. This was a particularly attractive idea to me, for at that time, the question of a mechanism of the Walden Inversion had not been completely settled. About thirty different theories had been proposed to account for it, and it seemed to me that, if we could get an inversion with an octahedral model rather than a tetrahedral one, we might be able to rule out some of the theories which had been advanced for the inversion in reactions of the tetrahedral organic molecules.

"While I was still pondering on it, Robert Auten came to see me, looking for a senior research problem. ... During his freshman year, he had been in my lecture class and was so well pleased with my ability as a teacher that he would like to do his research with me. I suggested the Walden Inversion problem. He was quite skeptical about it, but agreed to give it a try. Interestingly enough, when he used silver carbonate in place of potassium carbonate, he did get the *levo*-carbonato complex; that is, there was an inversion in the reaction with either potassium [carbonate] or silver carbonate. We learned some time later that the inversion did not take place because of the substitution of silver for potassium, but that it took place because we were dealing with basic reagents.

"Robert Auten proved to be an extremely valuable student and an ingenious research man. Werner had published very specific directions for the optical resolution of the dichloro-bis-ethylenediamine-cobalt(III) ion, using bromcamphor-π-sulfonic acid as the resolving agent [22]. When Auten repeated the experiment, he got no precipitate of the desired enantiomer at all. Two or three repetitions of the experiment gave no better result. He then reasoned that, since Werner was a European, his laboratory was probably somewhat cooler than ours. That would be especially true if Werner had carried out this resolution in the winter. Bob, therefore, repeated the experiment with the solution cooled to 16°C. This gave exactly the result which Werner had reported. I owe a great deal to Robert Auten, for it was this piece of my work that originally caught the attention of the chemical public."

This first analogue of a Walden inversion among inorganic compounds, sometimes now called a Bailar inversion, was published in 1934 as the first article [B13] in a 37-part series, "The Stereochemistry of Complex Inorganic Compounds" [B19, B20,B26,B27,B35,B36,B54,B55,B61,B69–B71,B74,B75,B78,B81,B87–B89,B97,B108, B109,B111,B114,B120,B141,B144,B153,B158–B160,B165,B166,B218,B231,B258], which extended over 51 years. Although it was later shown that the inversion proceeds by a mechanism different from that originally proposed, near the end of his career John still regarded this work as being his most significant scientific achievement. In 1989 he said, "It opened up a field. One doesn't often have the opportunity to do that" [18]. John's interest in inversion reactions continued throughout his long career [B36,B144,B147,B159,B162,B169].

TEACHING ACTIVITIES

John spent his entire academic career at the University of Illinois, where he remained for 63 years, almost half the time that the university had been in existence. He rose through the ranks, being Instructor (1928–1930), Associate (1930–1935), Assistant Professor (1935–1939), Associate Professor (1939–1943), Professor (1943–1972), and Professor Emeritus (1972–1991). As longtime Head of Illinois' huge Freshman Chemistry program, following Hopkins' retirement in 1937, he had 75–100 graduate students teaching at all times under his supervision. He also served as Departmental Secretary (1937–1951), Head of the Division of Inorganic Chemistry, which included both general and advanced chemistry (1941–1967), Head of the Student Placement Office (1937–1951), and a member or chairman of more than a dozen committees. In addition, John was in charge of the department's Summer Session, microanalytical laboratory, and machine shop. Together, these duties required working twelve hours a day and conducting research at night. In 1951, he reluctantly abandoned some of these roles because, as he put it, "I couldn't do it all and still be a research chemist and teacher" [18].

John's accomplishments in chemical education are almost impossible to summarize. He was a teacher of the highest level and guided many thousands of students through general chemistry; his lectures were models of clarity, organization, imaginativeness, and inspiration. A colleague described him as someone who "had a way of bringing out the best in each of the students who came his way. John was a patient man, but demanded in the end that the result was one of high quality. He always looked to educating the students beyond mere chemistry. He was concerned that the whole person be educated" [2].

No one will know how many hours taken out of how many busy days were spent in helping students, but many men and women owe their careers to the help, advice, and sympathetic understanding given by John Bailar. In his position as Director of the Student Placement Program, he assumed responsibility for job placement at all levels (bachelor, master, and doctor), a time-consuming but fascinating aspect of his career because it permitted him to get to know students personally. Each year, John helped more than 200 young chemists find employment. According to Larry Faulkner, former Head of the Chemistry Department, "Not only has he been a major force in the department, he also has a very special relationship with alumni. He has a phenomenal memory. He never forgets a name or a face" [18].

John was careful not to allow his research to interfere with his teaching, to which he devoted considerable time and thought:

> "I would throw away my notes after every lecture so that I wouldn't do the same thing the next year. I tried to talk about things that would interest students, to help them see the connection between chemistry and everyday life" [18].

One of the standard lecture demonstrations that John performed for his undergraduate students was the reaction between oxygen and hydrogen in a loosely stoppered iron tube. When the mixture was sparked, the resulting explosion would propel the stopper some distance. The "cannon" was always aimed up the center aisle of the large lecture hall, and if nothing else, the noise and the flying stopper would wake up any students who had fallen asleep. But on one occasion, the stopper, instead of zipping up the aisle, made a beeline for one of the teaching assistants, Miss Florence Leota Catherwood, who was a graduate student working under the direction of the biochemist (and discoverer of threonine) Prof. William C. Rose (1887–1985) [23,24]. Miss Catherwood, a versatile and capable young lady, absorbed (clunk!) the impact energy of the demonstration [7]. The students thought that this was very amusing, but it was considerably embarrassing to her, and John, always sensitive to others' feelings, apologized and offered her consolation. And console her he did, for on August 8, 1931 John and Florence began a long and happy marriage that lasted almost 44 years, until Florence's death on March 13, 1975. They were the parents of two sons, John Christian Bailar, III (born October 9, 1932), a physician and government official, currently Professor in the School of Medicine at McGill University, Montreal, Canada, and Benjamin Franklin Bailar (born April 21, 1934), educator, corporate executive, former Postmaster General of the United States (1975–1978), and currently Dean of the Graduate School of Administration at Rice University, Houston, Texas. After a year's mourning for Florence, on June 12, 1976 John married Katharine (Kay) Reade Ross, a family friend whom he had known since childhood (Kay had been his babysitter).

WARTIME ACTIVITIES

John was a consultant to several industrial companies and government laboratories, and during World War II he served as Official Investigator for the U.S. National Defense Research Committee (N.D.R.C.), devoting his efforts to studying screening smokes [P1] and nerve gases. In 1944, he was overseeing one of his students, Robert W. Parry, who was developing the fuel for a device that would generate colored smoke to aid in finding downed aircraft in the Pacific. Work had progressed quite rapidly, and a device meeting specifications was produced. A major test to demonstrate the device to top military leaders and officials of the N.D.R.C. was held in Urbana on the South Farm of the University of Illinois campus. The big moment came, and the smoke generator was ignited. For half an hour its performance was perfect; great clouds of bright red smoke rose up to high heaven. Everyone was delighted. But delight turned to apprehension when the generator emitted a large "puff" and a vigorous burst of red smoke. Things settled down for a few minutes, and people breathed a sigh of relief. Then a second "puff" suggested that all was not rosy. Finally, on the third "puff" the whole device suddenly became airborne and headed directly toward the assembled top brass, who, by ducking and scattering, escaped with their lives but with considerable loss of dignity. The "rocket" hit a tree, broke open, and burned quietly on the ground. Professor Fraser Johnstone, a top flight chemical engineer, a wonderful person, and Director of the University of Illinois Project, could not contain his disappointment. He went over to Parry, who had responsibility for the fuel, and made his displeasure clearly visible. When Johnstone stopped for breath, John, who never got excited, defused the tense situation by calmly telling Parry in the hearing of the disgruntled officials, "But Bob, you don't understand, you're supposed to kill the *other* side, not our own men."

On another occasion, in Parry's laboratory next door to John's office, a bottle of a smoke-generating fuel containing $FeCl_3$ picked up some of the atmospheric moisture for which Urbana is famous, and not only ignited but set off a number of neighboring bottles, filling the room with smoke. John calmed down his distraught student by saying "Now Bob, let's see if we can get the smoke out." He also remarked about a book salesman waiting in his office, who promptly disappeared, "I don't think that he'll be back." John's books bore the yellow-brown stains as long as he had them.

BAILAR AS A MENTOR

John educated several generations of chemists (90 doctorates, 38 postdoctoral fellows, and numerous bachelor's and master's degree candidates). About half of these, inspired by his love of teaching, entered academia. The roll of his former students reads like a "Who's Who" of inorganic chemistry and chemical education. These so-called "Bailarites" have been exceptionally successful; many occupy high administrative or research positions at some of the leading universities in the United States and several foreign countries. John was a sort of lay "Abraham" for his field. He went forth and populated the land. During the 1960s, former Bailar students were so dominant among inorganic chemists on university faculties that it was sometimes disadvantageous to be one of them. Of those choosing to enter industry, a number became research directors of the most important chemical companies in the United States.

John's success as a research supervisor and teacher owed as much to his enduring human qualities as to his considerable chemical knowledge. John and Florence invited his students to their home where they were treated as family. Insight into his unique personality can best be gained from the tributes of those who worked

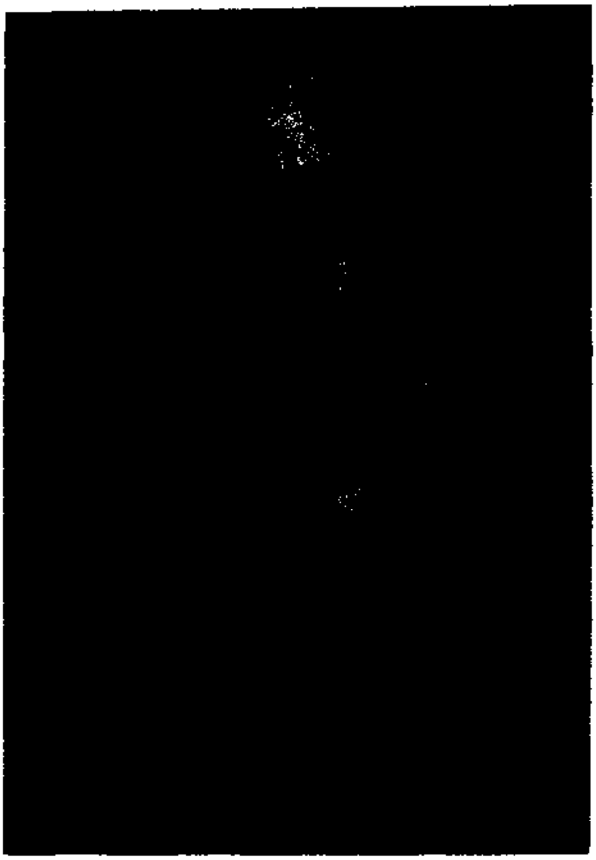

Fig. 4. At the University of Illinois, 1940s.

with him. According to Theodore L. Brown, "[John] was always there to listen, to offer such advice as I really asked for, and no more ... [He] always had time for others; his door was always open and he was always willing to lay down what he was doing to give his attention when he sensed that his visitor needed someone to talk to. [He] never (or almost never) raised his voice or showed strong emotion. ... John succeeded ... because he ... acted out of a rare selflessness. He just genuinely cared about others and would give as much of his attention and concern to a confused or troubled freshman student as to a graduate teaching assistant or to a faculty colleague. ... He was, most of all, a man who took pleasure in the successes and accomplishments of others, and who was glad of the chance to be of service, to be a friend."

One of John's former students, Stanley Kirschner, related an incident in which a new graduate student was unable to synthesize a coordination compound prepared by a previous student. Noting that the earlier student was an "ebullient extrovert" and the new student a "rather timid introvert," John recognized that the solution to the problem lay in the different manner in which these two types would operate a steam bath. According to Kirschner, the incident helps to "illustrate not only the scientific acumen of this great man, but his ability to observe personalities and make sound scientific judgments based on his observations, both scientific and human, and to treat people with extraordinary kindness and humanity [4].

At the memorial Service for John held on December 14, 1991 one of us (DHB) stated:

"My image of John Bailar was as a man bigger than most men, a sort of Samson of Science who opened great doors of opportunity through which many of us scurried onward to fulfilling careers in chemistry.

"He taught us that an original idea is among the most precious things in the world. [When, after a special topics course on metal chelate chemistry], I described a hypothetical molecule [a macrocyclic ligand] that I thought was interesting, he said, 'That's a good idea, why don't you make it?'

"He taught us how to survive in a competitive profession, for example, that publication should be prompt. When I described my work on a special classroom project, he said, 'Fine, write it up.' I hesitated, and he said, 'What is the matter?' I said, 'Well, I guess I'm not satisfied with these results yet,' and he said, 'Young man, do you think you will ever be satisfied with anything you do?'

"He taught us that the human value of a student is not related to how well that student can do in chemistry, that even though our careers as chemists depend on our research productivity, human values come first. I don't recall the circumstances, but when I was still a student, one day he said to me, 'Young man, chemistry is not as important to you as you think it is.'

"One of the guys invited everyone, including faculty, to his prelim party, and John came promptly and stayed for most of the designated time. No one drank any of the candidate's beer. I think that when John learned that he had this effect on students, he adopted the habit of carrying a glass of wine so that others would be comfortable in whatever was their normal behavior*. John was color blind and gender blind before such attributes were popular; everyone who came into his lab or his class or, otherwise into his range of responsibility, became his friend and, probably to him, one of his children."

SERVICES TO INORGANIC CHEMISTRY

When John began his career, not only coordination chemistry but inorganic chemistry in general was languishing in the doldrums. In the United States, inorganic chemists were exceedingly few, and most, like John, were overloaded with teaching

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* Although his sons never saw him drink when they were growing up, in later years, John and his wife would occasionally partake of a glass of wine.

duties in general chemistry classes. There were few inorganic courses beyond the freshman course, little inorganic research was being carried out, and avenues for publication were limited.

At the Fall 1933 ACS meeting in Chicago, five inorganic chemists, Harold S. Booth (1891–1950), Ludwig F. Audrieth (1901–1967) [25], W. Conard Fernelius (1905–1986), Warren C. Johnson (1901–1983), and Raymond E. Kirk (1890–1957), decided that there was a vital need for a series of volumes giving detailed, independently tested methods for the synthesis of inorganic compounds along the lines of *Organic Syntheses*, the series established by John's colleague at Illinois, Roger Adams. The five, soon joined by John, became the Editorial Board of the new journal, *Inorganic Syntheses*, the first volume of which appeared in 1939. Since its beginning, John was an active participant and motivating force in its affairs, contributing 16 syntheses [B28–B34,B48–B50,B64,B98,B241,B254–B256,B272] and checking five others [R1–R5], especially in the early years when the new journal required considerable support. He served as Editor-in-Chief of Volume IV (1953) [B77], and seven of his former students and three of his academic grandchildren (students of his former students) later served in a similar capacity.

In the American Chemical Society, a Division of Physical and Inorganic Chemistry was founded in 1908. John was active in the division, serving as Secretary (1948), Councillor (1949–1950), member of the Executive Committee (1948–1954), and Chairman (1950). However, in keeping with the growing importance of inorganic chemistry, John and a few of his colleagues felt that it merited separate divisional status, and they took steps to promote a Division of Inorganic Chemistry. When a physical chemist asked John why a separate division was necessary, he replied, "We need a forum for meetings, and, basically, we are just proud of our field." The physical chemist countered, "We already have many forums, and I don't really understand this 'pride thing', even though I am a member of the most important field of chemistry." John responded, "I can see that you *do* feel some pride in your field."

In 1957, the new division was finally established largely through John's efforts, and he served as the first Divisional Chairman [B271]. Similarly, the first journal in the English language devoted exclusively to the field, *Inorganic Chemistry*, began publication in 1962, again, largely through John's efforts. In short, the resurgence in the field after World War II, which the late Sir Ronald S. Nyholm [B204] called the renaissance in inorganic chemistry [26], owed much to John's pioneering labors.

RESEARCH

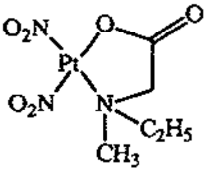
The sheer volume of John's research precludes our discussing any of it in great detail, but we can mention a few examples to give a glimpse of the broad scope of his interests and contributions. As we have seen, his work with Robert W. Auten on the inorganic Walden inversion [B13], carried out at a time when most chemists assumed that all the important work in coordination chemistry had already been done by Alfred Werner, arose from his interest in the stereochemistry of coordination compounds, which remained his primary interest throughout his long career. Although the exact research topics varied through the years, the problems investigated during the 1950s, when one of us (DHB) was a graduate student working in his group, are typical.

At the time, one of John's graduate students, Allan Gott, was completing a study on the resolution of the enantiomers of carboxylic acids using stereoselective chelation to a cobalt complex [B75]:

$$[\mathrm{Co}(l\text{-pn})_2(d,l\text{-tart})_2]^+ + l\text{-pn} \rightarrow [\mathrm{Co}(l\text{-pn})_3]^{3+} + l\text{-tart}$$

(liberated more rapidly than d-tart)

where tart = tartrate and pn = 1,2-diaminopropane. John Kuebler had just found that he could resolve a coordinated amino function, thereby removing an uncertainty in the literature concerning the stereochemical integrity of coordinated chiral nitrogen centers [B74]:



Incidentally, John Bailar was later (1962) to receive the John R. Kuebler Award of Alpha Chi Sigma, named after the father of his former student.

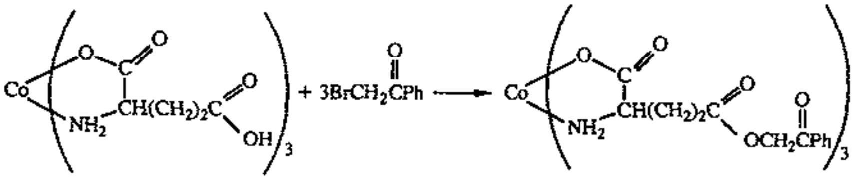
Basudeb Das Sarma was working with sexadentate ligands and showed that even Al^{3+} could yield enantiomers in such structures [B82]. Fred McCullough produced the diastereoisomers formed because of the *spiro* chelation of 2,2′-diaminobiphenyl [B88]. Daryle Busch showed that the tetrahedral beryllium complex with two moles of benzoylacetonate could be resolved into optical isomers, using an early form of chromatography on powdered quartz [B84]. He also resolved the $Co^{III}(EDTA)^-$ ion into optical isomers and demonstrated the bidentate and tetradentate character of $EDTA^{4-}$ in its Pd(II) and Pt(II) complexes [B81,B89].

At this time, John continued an interest in electrochemistry, both as a technique for the study of metal complexes [B57,B60,B62,B80,B85,B126] and as an area of application, particularly for the electrodeposition of metals [B46,B52,B83,B118]. Perhaps this dual interest shows, as well as any, how he was able to merge an involvement in chemistry as fun, an exciting intellectual adventure, with its application to the solution of problems useful to mankind. In John's laboratory there was never any arbitrary pecking order related to the distinction between basic and applied research.

John's electrochemical studies exemplify the synergistic combining of various investigators' talents. He collaborated with the analytical chemist Prof. Herbert A.

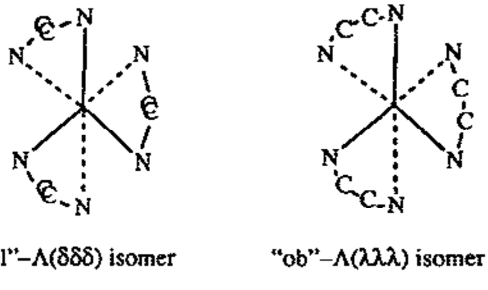
Laitinen (1915–1991) [2] in exploring the analytical or quantitative aspects of electrochemistry and with Prof. Sherlock Swann in investigating applied aspects of the field. For example, Bob Rebertus made a polarographic study of zinc–hydrazine complexes [B80], while Bob Rau studied the relationship between halogen-bridged, mixed-metal complexes and the electroplating of alloys [B118]. Ernie Lyons had joined John's group to complete his Ph.D. work after many years of experience with practical electrochemistry, and the two discovered a wide-ranging correlation between electronic structures of metal atoms and electroplating behavior [B83].

In addition to studies of stereochemistry and electrochemistry, the possibilities inherent in coordination polymerization, to which John and his students were to contribute so extensively, were glimpsed by John and Bill Drinkard during the 1950s [B96,B112]. Homogeneous catalysis and ligand reactions had not yet become recognized fields, but related problems arose constantly. John had assigned Philip Horrigan the problem of monoesterifying glutamic acid at the ω-position by chelating the α-carbonyl group:



The reactivity of an alcohol function β to a coordination site was investigated shortly thereafter [B116]. Thus the great capability of metal ions to control chemical reactions was apparent even at that early date, an example of the creative orientation of John's research group. New horizons were always in sight.

In 1959, with Illinois colleague and later (1990) Nobel chemistry laureate Elias J. Corey, John published a classic paper on octahedral trisdiamine complexes that led to applications of conformational analysis to coordination compounds [B108]. Central to their penetrating analysis was the relationship between chelate ring and ligand atom chiralities and the chirality due to helical chelation. Of the two diastereoisomers, the oblique (ob) and the parallel (lel) forms of tris-ethylenediaminecobalt(III) ion:

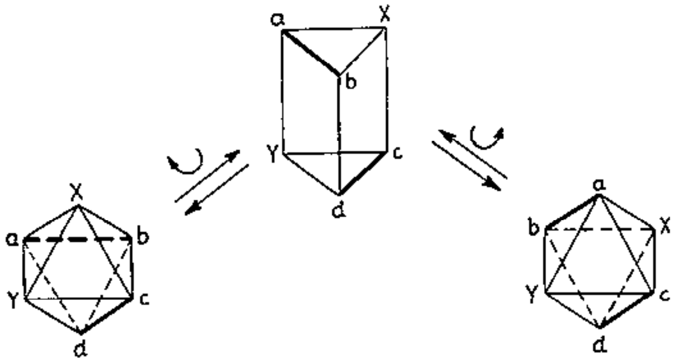


"lel"–Λ(δδδ) isomer "ob"–Λ(λλλ) isomer

the "lel" isomer occurs in an octahedral molecule of Λ helicity when the chelate rings all have the δ conformation. In this structure, the C–C axes are almost parallel to the three-fold axis of the complex ion. If the chelate rings are inverted to $\lambda\lambda\lambda$ while keeping the helical chirality of the complex fixed at Λ, the "ob" isomer is formed, and the C–C axes are now far from parallel (oblique) to the three-fold axis. The "lel" isomer was predicted to be more stable than the "ob". This and the other predictions of this early analysis have proven valid, and the extensions of the principles presented are enormous. Some idea of the broader aspects of stereochemistry can be gleaned from John's reviews of the topic [B17,B58,B147,B162,B169]. Also, many stereochemists have made use of his definitive article on the numbers and structures of hexacovalent complexes [B94].

John's best known contribution to our understanding of the dynamic behavior of coordination complexes is his discussion of the trigonal or "Bailar" twist. This mechanism accounts for the interconversion of cis and trans isomers of $[MX_2L_4]^{n+}$ compounds and for the racemization of $[M(LL)_3]^{n+}$ trischelates [B103]. He described this mechanism as follows:

"Consider, for example, the rearrangement *cis*-$[Coen_2XY]^{+n}$ into the trans form.



If the face of the octahedron cdY is kept in a fixed position while the parallel face abX is turned clock-wise through 60°, a triangular prism is formed. This should not require a great deal of energy, for if all of the angles formed by the donor atom–metal atom bonds remain equal, they have to change only from 90° to 81° 10′. ... If face abX turns through another 60°, the trans form of the original complex is obtained" [B103].

Although stereochemistry was always close to John's heart, it in no way bounded his interests and research activities. We have already noted his constant involvement with synthetic chemistry about which he wrote several reviews [B157,B201]. He identified a number of other goals with his synthetic efforts. Early on, the stabilization of unusual oxidation states was a matter of interest [B38,B41]. Various types of ligands were investigated because of curiosities related to their bonding capabilities: the effect of chelate ring size [B45], chelation by azo dyes [B73, B76, B264], chelation by and hydrolysis of Schiff base linkages [B79, B92, B123, B152, B164, B173, B193, B212, B215, B244], ligands that span trans positions [B218], the coordinating properties of a chelating biphosphine [B117], a chelating biarsine [B188], β-diketones [B130, B132, B134, B135, B148, B191], thioethers [B217, B235,B255,B256], and multidentate amines [B81, B82, B86, B89, B98, B114, B128, B136, B150, B151, B153, B158, B159, B165, B166, B178, B186, B187, B218, B238, B252, B265–B268,B277,B278].

Inorganic polymers were a research subject to which John and his group devoted considerable time and effort. John and his students provided examples of each of the three fundamentally different synthetic approaches that lead to chelate polymers [B125]. The first involves reactions of metal ions with bischelate ligands [B130]. The second mode of chelate polymerization involves chelation of metal ions by an existing polymer [B123,B129,B143]. The third reaction involves the polymerization of metal chelates containing free functional groups [B135,B145,B190]. Largely due to John's efforts, the chemical aspects of inorganic polymerization reactions are now fairly well understood [B96, B101, B104, B107, B112, B115, B121, B123, B125, B129–B131, B135, B143,B145, B190, B228]. The problems of achieving great thermal stability, high molecular weights, and suitable plasticity remain to be solved.

In a series of publications in the 1960s, John investigated the selective homogeneous hydrogenation of di- and triolefinic species, with particular emphasis on the application of the reactions to soybean oils [B156, B163, B170–B172, B174–B176, B180–B182, B192, B195, B203, B207]. Soybean oil, a mixture containing mainly glycerol esters of long chain organic acids, typically contains 7.5% linolenate, 50% linoleate, 27% oleate, 4% stearate, and 10% palmitate, though samples may differ in composition. The unsaturated compounds contain cis double bonds. The linolenates impart a bitter taste to the oil, while palmitates and stearates are difficult to digest. Ideal upgrading would involve converting linolenic esters (three double bonds) to linoleates (two bonds) or to oleates (one double bond) by selective hydrogenation with relatively little production of the saturated stearate ester. The catalysts studied were based on Ni, Pd, or Pt halides with phosphines or arsines as ligands and, as an especially important component, $SnCl_2$. Although the general catalyst system had first been reported by Cramer and his associates, John's studies have been both significant for their basic chemistry and highly promising in regard to the practical problem. For example, a sample of soybean oil, after hydrogenation, showed 80% monoene and 3% diene with no increase in the amount of stearate and no unreduced triene. Some side reactions occur as well: the unreduced double bonds are isomerized largely to trans configurations, and the residual unsaturation appears at various positions in the product molecules. In 1972, John summarized the catalytic reaction:

"[The catalysts] convert cis double bonds to trans double bonds. They cause double bonds to move along the hydrocarbon chain, probably in a random fashion, until double bonds become conjugated. They bring about the hydrogenation of all but one double bond; if further hydrogenation takes place it is extremely slow. Under properly selected conditions, they do not bring about hydrogenation, but only isomerization to the conjugated system. They cause ester exchange reactions [and] they ... can be recovered after hydrogenation and are still effective."

It is worth noting also that John was an early pioneer in the attachment of homogeneous catalysts to solid state supports, a method that he called the "heterogenization" of homogeneous catalysts [B207,B210,B211,B216,B227,B228]. This method has since become popular for a variety of catalytic applications because of the easy separation of the catalyst from the products at the end of the reaction.

Other topics investigated by John and his students include the resolution and studies of optically active complexes of various coordination numbers and configurations[B19,B20,B26,B27,B35,B36,B54,B55,B69–B71,B75,B84,B87,B88,B90,B97,B108, B120,B141,B144,B153,B158,B159,B165,B179,B202,B242–B244,B258,B259],kinetics [B95,B138,B150,B185], infrared spectra [B113,B188,B213,B215], catalysis [B25, B43, B79,B132,B156,B163,B174,B181,B192,B195,B203,B205,B209,B226,B230,B232,B234, B239, B248–B250], and reactions of coordination complexes in the solid state [B198, B200,B202,B222,B259,B260,B265–B268].

Over his long and fruitful career John published a total of 338 contributions to the scientific literature, and among these are two patents and 58 book reviews. Besides his numerous articles and other shorter publications, John wrote, co-wrote, or edited ten monographs [B77,B91,B208], texts [B47,B65,B146,B233,B240], or laboratory manuals [B12,B59]. His 834-page book *The Chemistry of the Coordination Compounds* [B91], written with 24 of his former students, summarized almost every aspect of the field, which, largely due to his teaching and research, was attracting more and more scholars.

MEMBERSHIPS, HONORS, AND LECTURES

As evidence of the great esteem in which he was held by his fellow chemists, John was chosen for the highest office to which they could elect him, President of the American Chemical Society in 1959, a position later occupied by three of his former students, Robert W. Parry (1982), Fred Basolo (1983), and Clayton F. Callis (1989). In 1961, he received the ACS Award in Chemical Education (now the George C. Pimentel Award), which was later given to former students Robert C. Brasted (1973), Leallyn B. Clapp (1976), Robert W. Parry (1977), and Fred Basolo (1992). In 1964, he received the ACS's highest award, the Priestley Medal [B137], an honor later bestowed on his former student, Robert W. Parry (1993), and "academic grandson," Harry B. Gray (former Basolo student, 1991). In 1968, he received the Manufacturing Chemists Association Award for Excellence in College Chemistry Teaching, which was also awarded to his former students Hans B. Jonassen (1959), Robert C. Brasted (1971), Robert W. Parry (1972), Leallyn B. Clapp (1973), and

Stanley Kirschner (1984). In 1972, he received the ACS Award for Distinguished Service in the Advancement of Inorganic Chemistry, an honor shared with his former students Robert W. Parry (1965), Fred Basolo (1975), and Daryle H. Busch (1976).

Throughout his career John was active in the American Chemical Society. Besides his chairmanships of the Divisions of Chemical Education (1947), Physical and Inorganic Chemistry (1950), and Inorganic Chemistry (1957), he was Chairman of the Divisional Officers Group (1949), Chairman or member of numerous national committees, and Director (1958–1960). He was a member of Alpha Chi Sigma (from 1922), the National Research Council (member of various committees), the Electrochemical Society (1948–1962), the International Union of Pure and Applied Chemistry (IUPAC) (Treasurer, 1963–1971; Conference Delegate, 1959, 1961, 1963), Phi Beta Kappa, Sigma Xi, Phi Lambda Upsilon, and other scientific and fraternal organizations. He was an Honorary Fellow of the Indian Chemical Society (1974) and an Honorary Member of the Illinois State Academy of Sciences (1976) and the Chemical Society of Japan (1985). He was a member of the editorial or publication boards of 12 journals (*Bioinorganic Chemistry, Chemical Reviews, Inorganic Chemistry, Inorganica Chimica Acta Reviews, Inorganic and Nuclear Chemistry Letters, Inorganic Chemistry, Inorganic Syntheses, Journal of the American Chemical Society, Journal of Chemical Education, Journal of Inorganic and Nuclear Chemistry, Oriental Journal of Chemistry*, and *Revue de Chimie Minérale*) and the holder of honorary doctorates from the University of Colorado (1959), the University of Buffalo (1959), Lehigh University (1973), and Monmouth College (1983). He delivered innumerable lectures in North and South America, Europe, Asia, and Australia, he held more than a dozen lectureships, and he was a visiting lecturer at five US (Colorado College; the Universities of Arizona, Colorado, and Wyoming; and Washington State University) and three foreign universities (Kyushu University and the Universities of Guanajuato and São Paulo). In addition, he served as a plenary lecturer at four international Conferences on Coordination Chemistry (Rome, 1957; Krakow, 1970; Moscow, 1973; Boulder, 1977).

In addition to those previously mentioned, John's numerous honors include the Frank P. Dwyer Medal (Royal Society of New South Wales, 1965), the J. Heyrovský Medal (Czechoslovakian Academy of Sciences, 1978), the Monie Ferst Award for Education through Research (Sigma Xi, 1983), and the Chernyaev Jubilee Medal (Kurnakov Institute of Moscow, 1989).

John was the first recipient of the University of Illinois' John C. Bailar, Jr. Medal, named in his honor, and his alma mater, the University of Michigan, named him Distinguished Alumnus for 1967. In recognition of his inestimable contributions to coordination chemistry, the Schweizerische Chemische Gesellschaft in Zürich, on September 3, 1966 at the centennial celebration of Alfred Werner's birthday (IX ICCC), presented John with the only Werner Gold Medal ever to be awarded, a fitting tribute to the elder statesman and prime mover of American coordination chemistry [B169].

LATER YEARS

On the occasion of John's retirement, his students and colleagues established the Bailar Lecture and Gold Medal at the University of Illinois. This lecture series has included such distinguished speakers as Fred Basolo, Richard H. Holm, Earl L. Muetterties, George W. Parshall, Daryle H. Busch, Harry B. Gray, Robert G. Bergman, Jack Halpern, John D. Corbett, Lawrence F. Dahl, M. Fred Hawthorne, and Nobel Laureates Henry Taube and Jean-Marie Lehn [2].

John retired in 1972, but the only visible change in his work pattern was the fact that instead of the 12 hours daily that he previously spent in his office, he spent seven hours. After his retirement, John had offers of full salary and pension from other universities but chose to remain at Illinois, saying, "I taught here 44 years. I belong with the university" [18]. Although he no longer accepted graduate students, he continued to work with undergraduates and postdoctoral students [5]. At the end of a symposium held to celebrate his 80th birthday, he said, "You have to think young. I go along with Robert Browning, who said, 'The best is yet to be'" [2].

John's independent spirit never left him: for example, at the age of 83, during the trip and tour of China that he made to the 25th International Conference on Coordination Chemistry, where he presented a symposium paper on "History of Coordination Chemistry in the United States" [27], a topic that he was uniquely qualified to discuss, he insisted on personally carrying his own heavy luggage. As a result, he tripped on an escalator in Hong Kong's Meridien Hotel, a fall from which he got up unassisted. A mere six weeks before he died, John attended his last American Chemical Society meeting, where he was taken ill. Always ready with a humorous but profoundly philosophical comment, he confided to his Illinois colleague Alexander Scheeline while recovering from the pneumonia that he had contracted, "Life is full of surprises — eat your dessert first" [28]. John C. Bailar, Jr. passed away on the morning of October 17, 1991 of a sudden heart attack. We shall not see his like again.

We think it appropriate to conclude this tribute to John with a quotation from one of his lectures, which truly captures the essence of the man:

> "My 50 years of teaching have been a continuous source of inspiration and joy to me. There is nothing more satisfying than to watch a young person's understanding broadening, to see the look of pleasure on his face when a new idea strikes home. Whether the student be a freshman or a graduate student is not important; the growth of the mind is still there. I am, of course, especially interested in those who have done their doctorate theses with me, for I know them better than the others. Nearly all of them have been highly successful, either as teachers and researchers, or have achieved high places in chemical industry. But many of those who sat in my classes during their freshman year have remained my close friends over the years and have brought me great happiness."

Fig. 5. Retired but still active, 1970s.

Fig. 6. Four generations of John C. Bailars (III, V, IV, II, from left to right), Christmas 1989.

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POSTDOCTORAL ASSOCIATES

1	Adams, Robert W.	[B181,B182]
2	Badar-Ud-Din	[B127]
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6	Bauer, Robert A.	[B214,B219]
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26	Patel, Kantilal S.	[B191,B193,B196,B212,B215]
27	Reinbold, Paul	
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33	Thabet, Samir	
34	Uden, Peter	
35	Uehara, Akira	[B249,B250]
36	Valent, Aladar	
37	Vassilian, Asbed	[B239]
38	Yoshikuni, Tadatsugu	[B248]