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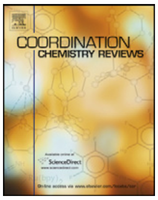

Preface

Elena and I were both drawn to the University of Kansas during the summer of 1992 by the prospect of working with Daryle Busch. Elena and her husband Alexander Kolchinski, already accomplished students of macrocyclic chemistry, were relocating from Kiev, Ukraine to work with the man whose contributions to macrocyclic chemistry they had carefully studied and long admired. I, knowing only that I liked inorganic chemistry and someday wanted to teach, had chosen the University of Kansas because my undergraduate advisor, Kim Lance, had assured me that Professor Busch was an exceptionally kind and inspiring mentor. Kim kept emphasizing that "you can't go wrong with Daryle" and, as usual, he was right. I spent my first year as a student in Lawrence discovering how influential Daryle was in the world of chemistry while, at the same time, marveling that someone so accomplished could also be so genuine, approachable, and generous of spirit. Throughout five thoroughly enjoyable years in Lawrence and onward into our careers, Elena and I have admired Daryle's uncommon blend of influence and humility, drive and patience, scientific vision, and confidence in others. In the fall of 2004, Elena, Kristin Bowman-James, and I had the opportunity to honor Daryle with a symposium and research group reunion to celebrate the first 50 years of his academic career. This event, like the many wonderful Busch group reunions that preceded it, was a heartwarming reminder of the broad and positive impact that Daryle has had on his students and colleagues. Although many professors are intelligent, generous and kind, few have shaped their fields of study and earned the respect and friendship of both their colleagues and students to the extent that Daryle has. Not long after the Busch symposium, I found myself helping with a freshman honorary induction ceremony on our campus. The ceremony follows a formal script with more than a few odd phrases, but I was suddenly impressed with the pamphlet's insightful description of character. "Character," it said, "is the foundation of responsibility and success... The qualities of character which we emphasize are: truth and helpfulness in our relations with others, courage in the maintaining of principles, constructive thinking..., and, most of all, charity in judging the actions of others." It is Daryle's depth of character and his charity in working with others over the past 56 years that again bring colleagues and friends together to celebrate a milestone in his career – his now slightly belated 80th birthday – with this special issue of *Coordination Chemistry Reviews*.

This project was initiated by Kristin Bowman-James and Barry Lever and we are indebted to them for this opportunity to celebrate Daryle's career. The contributors are representative of the many students, postdoctoral associates, colleagues, and friends who have benefited from Daryle's wisdom, dedication, and kindness. Likewise, the topics of their contributions reflect the breadth and depth of Daryle's research interests—interests that he has described so eloquently in an earlier review, "The Compleat Coordination Chemistry—One Practitioner's Perspective" [*Chem. Rev.* 93 (1993), 847]. Daryle's contributions to the field are also celebrated in two earlier special volumes, the first a celebration of his 70th birthday [*Coord. Chem. Rev.*, 174 (1998), edited by Ken Takeuchi] and the other a celebration of his first 50 years in academia [*Advances in Inorganic Chemistry*, 59 (2007), edited by Kristin Bowman-James and Rudi van Eldik]. The following paragraphs describe how the authors of this volume are connected to Daryle and his work.

Macrocyclic chemistry, pioneered by Daryle at the beginning of his independent career, took central stage in his research program. The first rational template syntheses of macrocyclic transition metal complexes by the Busch group in the 1960s opened this fruitful area of research, which soon assumed a life of its own. Not surprisingly, macrocycles also feature prominently in this issue, and various aspects of their fundamental chemistry and applications are reviewed in contributions by Barefield, Fabbrizzi, Korybut-Daszkiewicz, Hubin, Archibald, Lindoy, and Delgado.

Daryle recalls that E. Kent Barefield was a stand out on the roster of new graduate students when he arrived at Ohio State in 1965 and that he proved to be an even better student than advertised. Kent chose to work with Daryle and developed some of the very first metal-templated syntheses of azamacrocycles, an interest that he carried forward into his independent career. Daryle has often noted that Kent's way of making the ultimate macrocyclic ligand, cyclam, is still the best there is, except for the use of cyanide to liberate it from the nickel(II) ion which is not "green enough." (The guest editors note that they too have used this wonderful method and that the beautiful orange color of the complex is the next best thing to green.) Kent went on to a distinguished career in academe, first at the University of Illinois and then at Georgia Tech where he is now Associate Dean of the College of Sciences. Kent's review covers both historical aspects and exciting recent developments in the chemistry of important N-alkylated cyclam derivatives. Replacing the secondary amines of cyclam with tertiary amines affords complexes that are resistant to oxidation. One particularly impressive development in this area is the crystallization by Wonwoo Nam, Larry Que and co-workers of the first non-heme compound containing a $Fe(IV)=O$ moiety—a development made possible by the stability of alkylated cyclam derivatives.

Cyclam is also one of the favorite ligands of Luigi Fabbrizzi. Luigi Fabbrizzi became a friend and acquaintance of Professor Busch through what Daryle describes as "an inevitable confluence of the coordination chemistry traditions associated with the universities in Florence, Italy and Urbana, Illinois." Daryle has visited Luigi both

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at the University of Florence and at his current academic home in Pavia. Likewise, Luigi visited Kansas when the International Symposium on Macrocyclic Chemistry was held there in 1994. This past year Professor Fabbrizzi received the International Izatt-Christensen Award in Macrocyclic Chemistry in recognition of his creative research and we take this opportunity to congratulate him on this well deserved honor. (Three other contributors to this volume are also recipients of the Izatt-Christensen Award: Jean-Pierre Sauvage, 1991; Daryle Busch, 1994; and Jerry Atwood, 2000.) Luigi's review discusses the preparation, properties, and applications of azacyclam complexes. These molecules can be easily functionalized at a single site, thus making them particularly suitable for attaching anion receptors, redox switches, and other functional components. Modified azacyclam complexes serve as excellent building blocks for molecular devices.

Various kinds of macrocycle-based molecular devices are also described in the review by Bohdan Korybut-Daszkiewicz (now a Professor at the Organic Chemistry Institute of the Polish Academy in Warsaw), Renata Bilewicz, and Krzysztof Wozniak. Bohdan came to the Busch laboratory as a postdoctoral researcher in the late 1970s, when the group's efforts were focused on demonstrating the special advantages of oxygen carriers with protected cave-like sites that the group called lacuna. A later collaborative publication occurred during the Busch group's focus on the ligands called cyclidenes, which were developed because of their suitability as functional mimics for iron-based biomolecules such as myoglobin and cytochrome P450. Bohdan's contribution to this volume demonstrates that cyclidene-like tricyclic and polycyclic molecules are also excellent components of molecular devices.

Bisazamacrocycle ligands are the focus of a review by Tim Hubin and J.C. Timmons. Tim joined Daryle's group at the University of Kansas in 1995 and was among the early recipients of one of KU's Madison and Lila Self Graduate Fellowships. Tim became the graduate student member of the Procter and Gamble team that designed a very special peroxide bleach catalyst to remove stains from clothing without damaging or discoloring the fabric. Daryle notes that he accepted this challenge from P&G because it was obviously difficult, he thought he knew the main molecular design features necessary to produce the desired product, and because he could see Tim Hubin, Simon Collinson (another contributor to this volume), and himself forming the right team to do the job. According to Daryle, the rules for this challenge were tough: the metallic element had to be cheap and nontoxic; the complex containing it had to be extremely stable in hot basic media for times approaching an hour; and the catalyst also had to be highly selective, oxidizing only relatively reactive reductants. In his current work at Southwestern Oklahoma State University, Tim continues to design and prepare new macrocycles with catalytic and biomedical applications. By joining pairs of topologically constrained macrocyles together, Tim hopes to more than double their catalytic and biological activity. Tim often collaborates with another contributor to this issue, Stephen Archibald.

Functionalized azamacrocycles have already found numerous applications and show enormous promise for even more important uses in the future. Biomedical applications are highlighted in the review by Ryan Mewis and Steve Archibald. One field that particularly benefits from the high thermodynamic and kinetic stability of metallomacrocycles is medical diagnostics and imaging. For example, radioactive or fluorescent metal centers coordinated by macrocyclic ligands can function as reporters of biological molecular recognition events that occur selectively on the surfaces of tumor cells. Attaching molecular recognition fragments to metallomacrocycles that do not release their metal ions under physiological conditions is another challenging problem that is being addressed by a number of academic and industrial research groups. Steve Archibald, now Senior Lecturer at the University of Hull, worked with Daryle from 1995 to 1997 contributing extensively to the 3M project on photoproducts. Although Steve worked on the Busch group's most carefully guarded industrial collaboration during that time, group members enjoyed learning about various dinuclear, trinuclear, and polynuclear silver complexes as they were cleared for publication.

Leonard Lindoy joined the Busch research group as a postdoctoral member from Australia during the time when the group was busily defining the broad ranging possibilities of macrocycles as ligands. The most basic work had been established and other researchers had entered the field. This was a time when new goals were being defined. Daryle describes Len as "a natural leader who was instrumental in helping to redefine the goals and advances to be made with a new vision of the path forward." Professor Lindoy has continued to work with macrocyclic and supramolecular systems throughout his career and is author of a text: *The Chemistry of Macrocyclic Ligand Complexes*. Now Professor Emeritus at the University of Sydney, Professor Lindoy was recently awarded the David Craig Medal from the Australian Academy of Science for excellence in chemistry research. In their contribution to this volume, Lindoy, Meehan, Vasilescu, J.-E. Lee, and S.S. Lee review the chemistry and applications of pentadentate, dibenzo-substituted macrocyclic ligands that include hard and/or soft donor atoms.

While macrocycles were originally designed as excellent and selective ligands for metal cations, they can function equally well as receptors for neutral molecules or anions. The advantages offered by a cyclic or bicyclic host are even more important for anion recognition than they are for cation recognition because individual host–guest interactions are significantly weaker for anion binding than they are for transition metal complexation. In their contribution to this volume, Rita Delgado, Pedro Mateus, and Nicolas Bernier review the anion binding capabilities of seven polyammonium macrocycles and their cryptand analogs. Rita was a visiting researcher in the Busch Group during the late 1980s and contributed to the development of superstructured Schiff base oxygen carriers. She is now Head of the Chemistry Division of the Institute of Chemical and Biological Technology at the New University of Lisbon where she leads a research program in Coordination and Supramolecular Chemistry.

Daryle's interest in templates and molecular assembly extends beyond metal–ligand interactions into larger, supramolecular systems. Examples include the group's work in the 1980s on vaulted and supervaulted cyclidenes, which was directed toward bringing the macrocyclic complex, oxidant, and substrate together in a ternary system, and the group's preparation of a [3]-rotaxane in the late 1990s. Contributions to this volume by Sauvage, Atwood, and Meade involve self-assembled systems.

Jean-Pierre Sauvage and Daryle Busch became acquaintances and friends through their shared passion for the same realm of science. Each of these research leaders appreciates the contributions that the other has made to the area of template directed molecular assembly. The Busch group pioneered the concept of metal templates and was the first to successfully apply it to a simple yet elegant topological goal, the formation of rings. The first application of molecular templates to a topologically sophisticated issue, the tying of knots, was beautifully achieved by the Sauvage group. In their contribution to this volume, Sauvage, Durola and Wenger describe a group of non-hindered biisoquinoline chelates that have led to the preparation of novel [3]rotaxanes, [3]pseudorotaxanes, and molecular shuttles.

The careers of Jerry Atwood and Daryle Busch share some noteworthy parallels. Both are University of Illinois PhDs in Inorganic Chemistry; both moved to universities in the heart of the Midwest when their careers were at their peaks (Jerry to the University of Missouri and Daryle to the University of Kansas); and both are recent recipients of the ACS Midwest Award (Jerry in 2005 and

Daryle in 2008). Daryle suspects that the similarities also go a bit deeper and include a regional spirit of independence and perhaps also values. Daryle also notes that he has "been Jerry's fan since I first met him and watched him make new chemistry happen." In their contribution to this volume, Jin, Dalgarno, and Atwood describe recent advances in the assembly of novel metal-organic nanocapsules (MONCs).

As a graduate student in Daryle's group during the 1980s, Tom Meade took the cyclidenes to the limit, building on the outstanding work of many others, including Norman Herron, who made the first successful synthetic iron(II) dioxygen carrier with a cyclidene, and Ken Takeuchi, who modified the cyclidene structures and showed they can be made to bind substrates. It was Tom who first demonstrated the formation of ternary systems involving substrate and dioxygen bound within the same cyclidene cavity. In fact, doing at least three things at once seems to be a characteristic of this remarkable chemist as he is now associated with the departments of Chemistry; Biochemistry, Cell Biology, and Molecular Biology; Neurobiology & Physiology; and Radiology at Northwestern University. The contribution to this volume by Meade, Eckermann, Feld, and Shaw is a review of redox-active, self-assembled monolayers and the electrochemical techniques used to probe their electron transfer kinetics.

Harry Gray is the Arnold O. Beckman Professor of Chemistry and Founding Director of the Beckman Institute at CalTech. Harry's research interests include electronic structure of coordination compounds and mechanisms of inorganic reactions, subjects that he studied from the founders of these fields (Carl Ballhausen and Fred Basolo, respectively). Harry is currently applying his fundamental results in electron transfer mechanisms to a highly practical problem of harnessing solar energy. He is leading the NSF-funded Center for Chemical Innovation, "Powering the Planet." Harry's energetic, enthusiastic personality becomes inseparable from the conferences that he organizes and attends, including numerous Gordon Conferences where his presence transformed the pace and intensity of discussions. Harry continues to travel the country, giving invited lectures and seminars; the guest editors are happy to point out that he is particularly responsive to invitations from students. It is very fitting that Harry Gray's contribution to this volume (co-authored by Kyle M. Lancaster, James B. Gerken, Alec C. Durrell, and Joshua H. Palmer) concerns the impact of imidazole moieties, L = 2-(2′-pyridyl)imidazole (2-pimH) and 4-(2′-pyridyl)imidazole (4-pimH), on the electrochemistry of $[Ru(bpy)_2(L)]^{2+}$. All who participated in Busch group meetings during the group's development oxygen carriers know how much Daryle enjoys contemplating the electronic influence of well-chosen Lewis bases. (The guest editors suspect that Daryle continues to wear a calculator watch and carry a reference electrode conversion sheet in his wallet to ensure the accuracy of these musings.) Daryle describes Harry Gray as "the once-in-a-lifetime student of his spiritual brother, the late and great Northwestern University Professor Fred Basolo." Daryle and Fred Basolo followed similar career paths through Southern Illinois University and then John Bailar's group at the University of Illinois; it appears that these Illinois connections seeded both a tradition of leadership and lifelong friendships between Professors Busch and Gray and the late Professor Basolo. All three are past recipients of the University of Illinois' John C. Bailar Medal—Basolo in 1972, Busch in 1978, and Gray in 1984. Additionally, Gray received Northwestern's Basolo medal in 1994 and Busch received this honor in 2003.

At the most-fundamental level, all of the macrocyclic oxygen carriers and oxidation catalysts developed by the Busch group have been biologically inspired. Daryle is keenly interested in metalloenzymes (especially the ones that oxidize their substrates) and has remained closely connected to developments in bioinorganic chemistry throughout his career. This volume contains bioinorganic contributions from Ochiai, Riordan, and Yin.

Eiichiro Ochiai came to the Busch group at Ohio State University in the early stages of macrocyclic ligand development as a postdoctoral associate from Japan. Daryle recalls that Eichi explored the cobalt complexes of the group's new macrocyclic ligands as prospective vitamin B_{12} analogs. Ochiai's work showed that those complexes readily formed the σ-bonded organic derivatives characteristic of the vitamin. Along with another contributor to this volume, E. Kent Barefield, Eiichiro also studied the electrochemistry of macrocyclic nickel complexes with varying degrees of ligand unsaturation. Alongside his distinguished career at Juniata College and international appointments in Japan, Canada, and Sweden, Professor Ochiai has authored four texts on bioinorganic chemistry. The most recent, *Bioinorganic Chemistry: A Survey* was published in 2008. In his contribution to this volume, Ochiai provides a retrospective on the evolving field of bioinorganic chemistry and highlights some of Daryle's contributions.

Charlie Riordan, now Professor and recent former Department Chair at the University of Delaware, first became a friend of Daryle while a beginning faculty member at Kansas State University. In the early 1990s, Daryle (at the University of Kansas) had responded to an invitation to seek state-wide funding through EPSCoR (the Experimental Program to Stimulate Competitive Research). The proposal he designed included support of a postdoctoral researcher for every new Assistant Professor of Chemistry hired by a Regents University in the state of Kansas. Charlie was one of those professors. This and other features of the EPSCoR program were intended to build closer relationships between the chemistry departments in the state of Kansas, which had, in the immediate past, been more competitive that cooperative. The research and friendships seeded through Daryle's EPSCoR initiative continue to thrive and propagate as the original beneficiaries and their students have moved forward with their careers. Charlie has been deeply interested in developing ligands that can support novel reactivity. His tripodal, sulfur-containing analogs of the well-known tris-pyrazolylborates illustrate the potential of rational ligand design and selection in inorganic and bioinorganic chemistry. In his contribution to this volume, Charlie describes these ligands, the transition metal complexes derived from them, and applications of the complexes as models for zinc protein active sites and the activation of sulfur and dioxygen. Charlie's recent work opens an exciting new area that overlaps with many of Daryle's interests—dioxygen activation using nickel complexes.

Guochuan Yin completed his postdoctoral research in Daryle's group at KU and returned to China with a faculty position at the beginning of 2009. Daryle notes that Guochuan wanted his children to learn their native language at home because otherwise it would not be possible. There is too much to learn; too many kanji. Daryle describes Guochuan as his "first "graduate" to go home to China right away and with whom I continue to exchange information and work on publications" and adds that "this is neat." Guochuan was the last postdoc on the P&G project, a program in which he made spectacular discoveries, including the only known highly functional example of a transition metal catalyst within which metalhydroxo and metaloxo functions can be compared as the only variable in an otherwise identical system. These discoveries at KU are quite likely the inspiration for Guochuan's contribution to this volume which is an exploration of transition metal oxo and hydroxo moieties in redox enzymes and their synthetic models.

Daryle's keen interest in green chemistry, which culminated in his deep involvement in the ACS Green Chemistry Institute (where he is currently a Chair of the Governing Board), combined with his long-term interests in catalysis, resulted in highly productive collaborations with Bala Subramaniam, a well-known expert in chemical reactions in supercritical solvents. Bala Subramaniam and Daryle Busch were brought together as a team by a postdoctoral researcher in chemistry whose name appears on this document, now Professor Elena Rybak-Akimova of Tufts University. Elena wanted to do some experiments in super critical carbon dioxide and Professor Bala Subramaniam was known as the person who might be willing to make this possible. The introduction of the researchers was more successful than the first few experiments and Bala and Daryle were soon writing research proposals together. This eventually produced the Center for Environmentally Beneficial Catalysis, an NSF sponsored Engineering Research Center. After graduation from that source, CEBC is now a better funded KU Center of Excellence, with a dozen mostly giants of industry as partners, major industrial and state of Kansas funding, and multiple grant funding. It benefits from a continually growing infrastructure for process chemistry that is rare for a university campus. CEBC is also exceptional in its affinity to industry and its green chemistry and engineering capabilities. A review by Bala Subramaniam summarizes certain aspects of exciting chemistry that is being developed at the CEBC.

A review by Simon Collinson and W. Thielemans highlights current developments in two areas of great interest to Daryle: oxidation catalysis with transition metal complexes and environmentally sustainable chemistry. Postdoc Simon Collinson joined the Busch Group in 1995 as the more senior member of the team assembled to initiate the Procter and Gamble challenge to produce a catalyst that would enable them to compete with Unilever, a major rival that had just launched a peroxide bleach catalyst for the laundry detergent market. By this time macrocycles and modified macrocycles had been identified as key tools and Daryle had submitted a 2-page plan to P&G that Simon and Tim Hubin eventually brought to full productivity. In his independent career at Cranfield University, UK, Simon is interested in practical and efficient methods for converting biomass and recycled plastics into useful chemicals and materials. Coordination complexes of redox-active metals prove to be excellent catalysts for the oxidation of major biomass components (cellulose, starch, and lignin) and these oxidation reactions can be used to achieve depolymerization and/or functionalization in addition to bleaching. Importantly, hydrogen peroxide can be used as an oxidant, generating water as a sole oxidant-derived byproduct. The use of biomass as a feedstock for fuels, chemicals, and materials is at the frontier of modern industrial chemistry.

Masaaki Kojima (Okayama University) and Naohide Matsumoto (Kumamoto University) were both members of Daryle's group at Ohio State during the years when the group was developing the cyclidene family of oxygen carriers. It is no surprise that the two of them have formed a team (along with co-authors Ryohei Kawamoto, Kunihiro Fujita, Hisashi Maruyama, Yukinari Sunatsuki, Takayoshi Suzuki, and Seiichiro Iijima) to celebrate Daryle's birthday with their submission to this volume. Professors Kojima and Matsumoto have co-authored 48 papers over their careers including one with Daryle—a key paper concerning the Co(II) cyclidenes. The triple helicate complexes described in the current review were inspired by Daryle's work with pyridylaldazine ligands in the late 1950s.

Daryle: On behalf of the numerous students and colleagues who have been inspired by your career and touched by your kindness, we wish you many more happy birthdays and continued success in your work at the University of Kansas and with the ACS Green Chemistry Institute. You continue to show us how to approach new areas of science, how to serve, and how to lead. May the kindness that you and Jeri have always so generously given be returned to you 100-fold.

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