GOLDEN YEAR FOR INORGANIC CHEMISTRY

ACS MEETING NEWS: Inorganic Chemistry turns 50, giving inorganic chemists a reason to pause and celebrate

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AT THE American Chemical Society national meeting in Denver late last month, inorganic chemists convened as they usually do at national meetings to share their latest research results, catch up with old friends, and make new connections. But one symposium in the Division of Inorganic Chemistry offered them something different this time: an opportunity to celebrate a milestone, that of the 50th anniversary of their journal, ACS's Inorganic Chemistry.

Most of the chemists drawn to the symposium weren't yet alive in 1962, the year Inorganic Chemistry came into existence. But a handful of them, already practicing their craft 50 years ago, had papers published in the fledgling journal's first volume.

"When Inorganic Chemistry was created, John F. Kennedy was President, and Vietnam was a far-off place that many Americans were just starting to hear about," said Richard Eisenberg, a chemistry professor at the University of Rochester and current editor-in-chief of Inorganic Chemistry, who opened the Symposium. "No American had yet orbited Earth, although two Soviets had," Eisenberg continued, raising some murmurs and nods from the standing-room-only audience. "The Super Bowl didn't yet exist," he added.

"Computers were large, clunky, and unreliable centralized machines—there was nothing personal about them," Eisenberg said, drawing more reactions from the crowd. "Webs were strictly for Charlotte and other spiders. The Internet hadn't been created—Al Gore was only 14 years old."

After the chuckles died down, Eisenberg reflected further about the journal's past, running through the lineage of editors: founding editor Robert W. Parry of the University of Michigan (1962-63); Edward L. King of the University of Colorado (1964-68); M. Frederick Hawthorne, now at the University of Missouri, Columbia (1969-2000); and himself since 2001. Eisenberg said it was during Hawthorne's 32-year reign that the journal "came into its own and grew to become the voice of inorganic chemistry."

The first paper in a new journal is usually reserved for someone special, Eisenberg noted. For Inorganic Chemistry, that special someone was Northwestern University's Fred Basolo, a pioneer in metal-ligand coordination chemistry whose paper on the synthesis of rhodium, iridium, and platinum nitro complexes was the premier citation: Inorg. Chem. 1962, 1, 1.

THE JOURNAL published four issues that first year, totaling 977 pages. By 1964, the journal was being published monthly, and it became a biweekly in 1983. In 2010, its 49th year, the journal published 11,644 pages. The most prolific author so far is the late F. Albert Cotton, an inorganic chemistry icon from Texas A&M University, whose name appears on 614 papers in the journal—more than twice as many as anyone else.

The 50th anniversary symposium stretched over three days and featured nearly 50 speakers whose lectures highlighted key topics on which Inorganic Chemistry regularly publishes. These include synthesis, mechanisms, structure, bonding, and spectroscopy in areas ranging from biological and supramolecular chemistry to solid-state and materials chemistry to photochemistry and energy research. "As such, the symposium recognized the diversity of inorganic chemistry today," Eisenberg told C&EN.

That wasn't always the case. "In the early days of inorganic chemistry, the field was just growing and there was no dedicated place in the U.S. to publish new inorganic results," recalled Harvard University's Richard H. Holm. "There was the Journal of the American Chemical Society and some specialized journals for publishing inorganic papers, but the burgeoning field needed a home."

A handful of leading inorganic chemists of the day got together and petitioned ACS to start Inorganic Chemistry, Holm said. He was tipped off about the forthcoming journal by Cotton, who had been his Ph.D. adviser at Massachusetts Institute of Technology. "I remember thinking it would be important to have a paper in the first volume of the new journal," Holm related.

Holm, as a neophyte professor, published a paper on spectral and magnetic property changes in nickel(II) complexes upon switching ligand substituent groups, which appeared in the third issue of the journal...
That fundamental work was part of a series of papers by Holm's group that exemplified early research on coordination chemistry.
Fifty years on, Holm elaborated on his group's most recent paper in the journal, which also happens to be on nickel (II) complexes. The Harvard researchers have developed nickel (II) hydroxide pyridine-carboxamidates that trap carbon dioxide by binding and converting it into bicarbonate (Inorg. Chem., DOI: 10.1021/ic200942u).

**ONE TOPIC** that kept popping up throughout the symposium was Inorganic Chemistry's original plain-Jane yellow cover. The yellow page was unadorned except for the journal's name on a black field, the issue date listed at the top, and a nod to ACS as the publisher at the bottom. Most inorganic chemists have no other way to describe the original cover other than it was “particularly ugly,” Holm said.

“That's the way it was for the first 35 years,” Holm chided. At least when you went to the airport to pick up visitors, you could just hold a copy of Inorganic Chemistry instead of a piece of paper with a person's name on it, he said. “They would instantly know where to go.”

But times do change. Art was eventually added to the Inorganic Chemistry cover in January 1997. Holm had the distinction of supplying the graphic for that artistic endeavor. His group is known for preparing the first synthetic analogs of the active sites of iron-sulfur proteins, so he selected an iron-sulfur cluster compound.

Another evolutionary cover change came in 2001, when Eisenberg took the helm. The mellow yellow was replaced with an equally mellow green, and a modified design was introduced. The first green cover paid tribute to Hawthorne with an array of carbon rane structures from his research.

Although several symposium speakers published papers in Inorganic Chemistry during its first year, only one can claim a paper in the inaugural issue: Harry B. Gray of California Institute of Technology. Gray reminisced about his 60 years of work on metal oxo complexes, mixing in his signature off-the-cuff witticisms. Gray almost had the capacity crowd rolling in the aisles with his quips on bonding and structure that only inorganic cognoscenti would appreciate.

But Gray also mixed in some serious chemistry. His first paper in the journal described the electronic structure of the vanadyl ion, VO$_2^+$, featuring work carried out when he was a postdoc at the University of Copenhagen (Inorg. Chem. 1962, 1, 111). In that paper, and in a subsequent paper on chromium and molybdenum oxo ions published in the journal a few months later, Gray and his colleagues proposed an electronic structural model of multiple bonding in metal oxo complexes.

“The dianionic oxo ligand occupies a very special place in coordination chemistry,” Gray explained, “owing to its ability to donate π electrons to stabilize high oxidation states of metals.”

Those early papers included hand-drawn molecular orbital energy diagrams, he pointed out. “There weren’t any computer graphics back then,” he said. “These diagrams weren’t particularly pretty, but there wasn’t any other way to do it.”

Gray's work on metal oxo complexes led his group and others to better understand long-range electron transfer in metalloenzymes, in particular iron oxo complexes that serve as intermediates in oxidations catalyzed by cytochrome P450 and the likely role of manganese oxo complexes in the oxygen-evolving complex involved in splitting water to form O$_2$ in photosynthesis.

“We are running out of just about everything on this planet except seawater,” Gray observed. “We are going to have to figure out how to use something besides good old oil, natural gas, and coal to make chemicals and fuels.” He believes inorganic chemists have a bright future in making metal oxo complexes from simple starting materials, water, and sunlight and then using them to spawn the electrons and protons needed to generate solar electricity, fix nitrogen, and make fuels from carbon dioxide.

“That's what my lab is working on now,” Gray said. “Metal oxos are here to stay after 50 years.”

When it comes to evolving technology, the greatest impact on inorganic chemistry over the course of the journal's history has been in chemical structure determinations, suggested Northwestern University's James A. Ibers. From the vantage point of being an associate editor of Inorganic Chemistry in the 1960s, Ibers said the crystallography back in those days was often done by the seat of the pants.

“It was a time of discovery, with new types of molecules being reported with bonding that you never would have imagined,” Ibers recalled. “It was hard to know what was real and what was not real.”

The changes since then have been equally unbelievable, he pointed out. In 1962, in Inorganic Chemistry's first issue, there were 38 papers, and none presented X-ray crystal structures, although a few had powder diffraction results, Ibers noted. In the current volume, looking at the Aug. 15 issue, there were 64 papers reporting 44 crystal structures, he said.

“Clearly there has been a structural evo-
lution in single-crystal X-ray techniques for doing inorganic chemistry," Ibers stated. "There are two aspects to that: development of computation and instrumentation."

Computing power was still wanting in the early 1960s, Ibers said. For example, in 1962 the room-sized IBM 704 operated at a rate of about 500 instructions per second, he noted. The latest PC chips operate at about 50 billion instructions per second, a factor of 10^9 faster, he said.

"Fortunately, the crystallographic software in the early days had been worked out and came courtesy of the national laboratories," Ibers added. "It was all open-source programming, which meant you could modify it. And I sure did modify mine for a variety of purposes, because with the limited computing power it was necessary and depended on the compounds you were working on. But today the software code is all set, and you bow to those who write it."

On the instrumentation side, X-ray diffractometers once used cameras with real photographic film, and the images had to be judged manually by eye, Ibers explained. Nowadays, instruments have charge-coupled device cameras as detectors that produce digital data—"it's electronic film," he said. In addition, the software programs now read and process the data, helping to prevent scientists from making mistakes.

Ibers is one of the most prolific publishers in Inorganic Chemistry, with 245 papers to his credit. His first paper in the journal came in 1964 when he was at Brookhaven National Laboratory. It centered on the crystal structure of sodium peroxydecahydrate, Na₃XeO₄•8H₂O (Inorg. Chem. 1964, 3, 1412).

He also helped Eisenberg publish his first paper in the journal in 1965, when Eisenberg was a graduate student at Columbia University. Eisenberg was learning crystallography from Ibers at Brookhaven, and they teamed up to determine the crystal structure of a nickel(II) bis(dithiolat) complex (Inorg. Chem. 1965, 4, 605). Eisenberg's latest work, which he presented during his symposium lecture, features a cobalt bis(dithiolat) complex that is a highly active catalyst for both visible-light-driven reduction and electroreduction of protons to generate hydrogen in water-splitting reactions (J. Am. Chem. Soc., DOI: 10.1021/jacs.2b07842).

Ibers now studies solid-state reactions and the subsequent structural changes in metal oxides, sulfides, selenides, and tellurides, focusing on thorium, uranium, and neptunium compounds. His most recent paper in Inorganic Chemistry, on the structures of neptunium thiophosphates such as NpPS₄, came out during the ACS meeting (Inorg. Chem., DOI: 10.1021/acs.inorgchem.1c01493).

AS THE LAST speakers were unplugging their computers—not tucking away their overhead transparencies as they would have done 50 years ago—Eisenberg reflected on the symposium. "I think this was a dazzling program," he said. "It included many of the leading chemists associated with the journal since its inception, scientists whose names have become synonymous with inorganic chemistry. This symposium was very powerful in showcasing the many dimensions of inorganic chemistry, from biochemistry and environmental science to materials science and solar energy conversion. We know there's still a lot more to come."