Periodic TableTalks: The Elements Never Go Out of Style

Javier Vela
Iowa State University, vela@iastate.edu

Emily A. Weiss
Northwestern University

Follow this and additional works at: https://lib.dr.iastate.edu/chem_pubs

Part of the Inorganic Chemistry Commons, and the Materials Chemistry Commons

The complete bibliographic information for this item can be found at https://lib.dr.iastate.edu/chem_pubs/1309. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.

This Article is brought to you for free and open access by the Chemistry at Iowa State University Digital Repository. It has been accepted for inclusion in Chemistry Publications by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Periodic TableTalks: The Elements Never Go Out of Style

Abstract
With the cancelation of the Spring ACS National meeting in 2020—and subsequent in-person meetings—because of the COVID-19 pandemic, the Division of Inorganic Chemistry (DIC) sought new ways to connect with its membership and continue to showcase the fantastic research carried out by inorganic chemists. The DIC executive committee thus initiated monthly Zoom webinars with two speakers each, typically one junior investigator and one more-established researcher, selected with input from each of the DIC subdivisions: Bioinorganic, Coordination, Solid-State, Organometallic, Nanoscience, and Sustainable Energy & Environment.

Disciplines
Inorganic Chemistry | Materials Chemistry

Comments
This document is the unedited Author's version of a Submitted Work that was subsequently accepted for publication in *Inorganic Chemistry*, copyright © American Chemical Society after peer review. To access the final edited and published work see DOI: 10.1021/acs.inorgchem.1c01094. Posted with permission.
Periodic TableTalks: The Elements Never Go Out of Style

With the cancelation of the Spring ACS National meeting in 2020—and subsequent in-person meetings—due to the COVID-19 pandemic, the Division of Inorganic Chemistry (DIC) sought new ways to connect with its membership and continue showcasing the fantastic research carried out by inorganic chemists. The DIC executive committee thus initiated monthly Zoom webinars with two speakers each, typically one junior investigator and one more-established researcher, selected with input from each of the DIC subdivisions: Bioinorganic, Coordination, Solid-State, Organometallic, Nanoscience, and Sustainable Energy & Environment.

Named “Periodic TableTalks” and open to all—not just DIC members—these presentations have been immensely successful and well-received. Two to three hundred people from across the world registered for each TableTalk. The webinars were recorded and made available to those registered who could not attend. TableTalks attract a range of attendees, from undergraduate students to seasoned and retired investigators. We had attendees from as far as Australia, along with students at undergraduate institutions and students currently enrolled in Inorganic Chemistry courses.

We are happy to highlight research contributions from the first season of TableTalks speakers in this Inorganic Chemistry Virtual Issue. Below we present a synopsis of each speaker with references to their articles. The Virtual Issue includes these articles that appear in Inorganic Chemistry and other ACS journals of special interest to the DIC membership.

**Robert J. Gilliard, Jr.** and his group at the University of Virginia are key players in the renaissance we are witnessing in the organometallic chemistry of alkaline-earth elements. In collaboration with David J. D. Wilson from La Trobe University in Australia, Gilliard reports the stepwise reduction of (carbene)MBr(L) and (carbene)M(L) complexes, where M = Be or Mg and L is bpy or a 1,4-disubstituted diazabutadiene.\(^1\) Critically, the doubly-reduced alkali-earth complexes exhibit strong π-bonding across the entire carbene–M–L core, thus featuring a rare s-block heterocycle.

Building on this significant expansion of the redox chemistry of the group 2 elements, Gilliard and Charles Edwin Webster from Mississippi State University report monomeric magnesium cations of general formula \([\text{NHC}]_3\text{MgR}^+\), where R = Me or Br.\(^2\) Crystalllographically characterized as their Br or BAr\(^F\(_4\)) \((\text{Ar}=\text{3,5-bis(trifluoromethyl)phenyl})\) salts, these unique organomagnesium cations form by Schlenk-type rearrangement and benefit from untethered stabilization of multiple carbenes. Based on the steric hindrance around the NHC, the magnesium centers are either four- (tetrahedral) or five-coordinate (trigonal bipyramidal).

In collaboration with Gernot Frenking from Philipps-Universität, Gilliard also reports salts of the paramagnetic beryllium radical cation \((\text{CAAC})_2\text{Be}^+\), where CAAC is a cyclic (alkyl)(amino)carbene.\(^3\) Isolated from the mild oxidation of the zero-valent analog with TEMPO \((2,2,6,6\text{-tetramethylpiperidin-1-oxyl})\), and characterized by elemental analysis, X-ray crystallography, EPR, and Density Functional Theory (DFT), \((\text{CAAC})_2\text{Be}^+\) is a lone example of a charged s-block radical and compound in which beryllium resides in a formal +1 oxidation state.

**Oleg Ozerov** and his group at Texas A&M University have a handful of new developments in the organometallic chemistry of the transition metals. They explore the degree of electronic
communication between diarylamido/bis(phosphine)(PNP)-coordinated group 10 metals bridged by ynediyl linkers. Using cyclic voltammetry, UV–Vis–NIR ground-state absorption, and EPR spectroscopy, X-ray crystallography, and DFT, they show that the degree of delocalization in the monooxided mixed valence cations increases for 1,6-bis(ethyne)phenyldiyil < butadiynediyl < μ-ethynediyl and Pd < Ni ≤ Pt. The Robin–Day classification of these compounds ranges from nondelocalized (class I) for M = Pd with 1,6-bis(ethyne)phenyldiyil linker to borderline delocalized (class II/III) for the Ni and Pt with μ-ethynediyl linkers, which can be explained based on the competition between the physical proximity of the two redox sites and the strength of their orbital interactions.

Early metals are full of surprises, and Ozerov shows that the pincer complex (PBP)Ir(CO)₂ adds O–H, N–H, or F–H bonds in water, alcohols, phenols, benzoic acid, or triethylamine trihydrofluoride across the boryl–iridium unit. Reaction with alcohols proceeds by initial protonation of the basic Ir center, while reaction with amines requires precoordination of the basic nitrogen to the acidic B center. Ozerov also reports PBP and PAIP pincers of Rh containing a central bis(N-pyrrolyl)boryl or -aluminyl unit. Attempts to remove pyridine from the four-coordinate Al site in (PAlpyP)Rh(CO)₂ through abstraction with BF₃·Et₂O resulted instead in B/Al metathesis to produce (PBP)Rh(CO)₂. Because this preserves the pincer structure, similar transelementation reactions may enable templating pincer complexes of other main-group elements.

Lisa Fredin and her theoretical and computational group at Lehigh University collaborate with Maria Abrahamsson from Chalmers University to demonstrate the unique excited-state dynamics of Ru(II) complexes with quinoline-pyrazole ligands. At 77K, these complexes convert to triplet MLCT states that live for microseconds, but decay from this triplet differently depending on whether the ligands are tridentate or bidentate. A subset of complexes undergoes photoinduced ligand exchange with solvent or Cl⁻ or photoinduced ligand dissociation and coordination of multiple Cl⁻. Fredin uses DFT to understand the relative stabilities of states within these complex potential energy profiles.

In work with Lund University in Sweden, Fredin describes her calculations of excited-state potential energy surfaces of two bis-tridentate Ru(II) complexes and their relationships to excited state lifetimes, and, in particular, to differentiate the decay pathways of electronically and geometrically similar complexes. Fredin highlights the importance of the number of available triplet MLCT conformations available in determining the lifetime of this state, a result only accessible through accurate calculation of multidimensional excited state surfaces.

James McCusker from Michigan State University demonstrates his breadth of expertise ranging from molecular photophysics to photochemistry and interfacial processes in electrochemical cells. McCusker and his group use time-resolved X-ray spectroscopy to probe the origin of the particularly fast (270 ps) excited-state relaxation of a low-spin Fe(2,6-
(dicarboxypyridyl)pyridine). K-edge X-ray emission spectroscopy establish the $^{5}T_{2}$ state as the lowest energy excited state and X-ray absorption fine-structure measurements indicate a highly anisotropic coordination sphere, which is consistent with the fast transition to the symmetric ground-state structure.

In another important contribution to the photocatalysis field, McCusker demonstrates the ability of a Fe(II)-trispyridyl complex to act as a photosensitizer for a series of benzoquinoid electron acceptors. This work shows that Fe(II) polypyrrolid complexes can participate in photoinduced electron-transfer reactions without involving MLCT states, which distinguishes them from the mode of action of analogous Ru and Ir complexes. McCusker also studies the influence of various passivating electrolytes on the structure and function of Fe- and Ru-based molecular photosensitizers within sensitized TiO$_2$ Graetzel-type photovoltaic cells. Spectroscopic characterization of the rate of electron exchange between the dyes and the TiO$_2$ allowed for selection of an electrolyte that increased the short-circuit current and efficiency of the cell by a factor of ten through cation intercalation into TiO$_2$.

**Geneva Laurita** from Bates College in Maine masterly uses neutron total scattering and pair distribution function (PDF) analysis to reveal the paracrystallinity of B-site cations in LaSr$_3$NiRuO$_8$. These are locally ordered within individual perovskite sheets—below 6 Å—but lack perfect registry across stacked sheets in three-dimensions—at 12 Å. This explains why some Ruddlesden–Popper (An+1BnO3n+1) phases that display antiferromagnetic behavior appear to lack B-site ordering when examined through traditional crystallography. As part of a multi-PI collaboration lead by Robin T. Macaluso from the University of Texas, Arlington, Laurita contributes to our understanding of the effect that stereochemically active Pb 6s$^2$ lone pairs have on the yellow-to-red thermochromism in the mixed-anion compound PbVO$_3$Cl.

Laurita and coauthors also present structural characterization of the ferroelectric pyrochlores along the series Cd$_2$Nb$_2$O$_{7-x}$S$_x$ (x = 0–0.7). Synchrotron diffraction experiments and first principles calculations shed light into how inversion-symmetry lifting displacements arise, how anion substitution controls covalent cation–anion interactions, and ways to tune polar behavior in the pyrochlore lattice.

**Arthur Mar** from the University of Alberta and Anton O. Olinsky—now at Manhattan College in New York—use machine learning to predict, with 95% accuracy, the site preferences or “coloring” of half-Heusler compounds based on 179 experimentally known structures and 23 descriptors. While cleansing their now publicly available model, Mar and coauthors find that size (radii) and metallic character, in addition to electronegativity, strongly influence site distribution. Critically, two compounds suspected of having incorrect site assignments, GdPtSb and HoPdBi were resynthesized and structurally characterized. The machine-learning predictions were
confirmed by single-crystal and powder X-ray diffraction, as well as by total energy configurations from first-principles calculations.

As part of a collaboration led by Jiyong Yao from the Chinese Academy of Sciences in Beijing, Mar contributes to understanding nonlinear optical behavior and second-harmonic generation in the quaternary chalcogenides AHgSnQ₄ (A = Sr, Ba; Q = S, Se).¹⁶

Back to the Heusler theme, Mar and his group build a machine learning model that predicts, with 98% accuracy, which full-Heusler compounds should exist based on known full-Heusler structures.¹⁷ Six of seven such candidates were successfully synthesized. This opens exciting opportunities for understanding ordering, determining the site occupancies, and preparing solid solutions between pairs of related half- and full-Heusler compounds.

Lisa Olshansky from the University of Illinois, Urbana-Champaign, presents work performed with Dan G. Nocera from Harvard University and JoAnne Stubbe from Massachusetts Institute of Technology. Olshansky and coworkers report a new photoactivated ribonucleotide reductase (photoRNR) in which photooxidation of a tryptophan (W) residue, replacing Y₃₅₆ within the α/β subunit interface, follows a stepwise electron transfer then proton transfer (ET/PT). The new construct achieves a threefold enhancement in photochemical yield of W· relative to F₃Y·, and a sevenfold enhancement relative to Y·. Olshansky and coworkers also reveal that some of the challenges associated with assay development are due to dynamic concentration-dependent and deoxynucleotide (ATP)-dependent interactions of the αs and αs/β subunits in E. coli la RNR.

In work with Andrew S. Borovik from the University of California, Irvine, and T. Don Tilley from the University of California, Berkeley, Olshansky uses a biotin-streptavidin approach to build artificial metalloproteins containing Co₄O₄ cubane clusters.¹⁸ These clusters display terminal and cofacial CoIII–OH₂ sites stabilized by hydrogen bonds, and their electrochemistry is affected by the presence of proximal residues and pH. Similar to the oxygen-evolving complex in photosystem II and to water-oxidation catalysts, these systems underline the importance of secondary sphere interactions in complex pH-dependent redox chemistry.

Patricia dos Santos and coworkers at Wake Forest University, in collaboration with Katherine A. Black from Weill Cornell Medical College, use kinetics measurements to show that the thioredoxin (Trx) system of Bacillus subtilis reduces protein persulfide intermediates during the synthesis of thio-cofactors.¹⁹ Interestingly, inactivation of thioredoxin A...
and its reductase impairs Fe−S enzyme activity, suggesting the involvement of the Trx system in Fe−S cluster metabolism.

**Raúl Hernández Sánchez** and coworkers at the University of Pittsburgh report the synthesis of a rare type of tubularene compounds with “zigzag” geometry. These carbon-based nanotubes consist of radially oriented \([n]\)cyclo-meta-phenylenes, with edge-sharing benzene rings built into the tubularene’s \(\pi\) -surface.

In one more tour de force in synthetic chemistry, working under Theodore A. Betley at Harvard University, Hernández Sánchez presents a combined redox, spectroscopic (\(^{57}\)Fe Mössbauer and NIR), structural, and magnetometry study of three octahedral \((L)_2Fe_6\) clusters supported by the all-nitrogen polycyclic cryptand \((L)\). Increasing the oxidation state of the \([Fe_6]\) core slightly decreases its volume and the average Fe−Fe distance. However, the Fe−N distances and Fe−N−Fe angles vary linearly with oxidation state. As the spin ground state of the \([Fe_6]\) core increases, so do the average Fe−N distances. The structural and spin states trends observed for the \([Fe_6]\) core in these complexes is rationalized based on one of the most fun molecular orbital diagrams in recent memory—a must see(!).

**Kara Bren** and her group at the University of Rochester show that buffer pKa plays a critical role in determining the exact mechanism when the hydrogen-evolution reaction (HER) is catalyzed by homogeneous complexes. Their studies show that with lower pKa buffers protonation of a cobalt(I) porphyrin peptide is fast, whereas with higher pKa buffers hydride formation becomes rate-limiting and is first-order in both buffer and catalyst.

In collaboration with Ellen M. Matson, also from the University of Rochester, Bren and coworkers report the catalytic reduction of aqueous nitrite to hydroxylamine and ammonium in near neutral pH. Controlled potential electrolysis of the molecular iron catalyst—supported by a pentadentate nitrogen macrocycle, FeN₅H₂—in the presence of nitrite at -0.98 V Ag/AgCl (1 M KCl) and pH 7.2 produces hydroxylamine with a faradaic efficiency of over 90%. Further, FeN₅H₂ catalyzes hydroxylamine disproportionation into ammonium, dinitrogen, and nitrous oxide.

In a perspective on engineered enzymes and bioinspired catalysts for energy conversion, Bren discusses relevant examples of proton, molecular oxygen, and carbon dioxide reduction, as well as of water oxidation, emphasizing the roles that proton transfer and second-sphere interactions play in these reactions.

**Alina Schimpf** and her group at the University of California, San Diego, have achieved the synthesis of colloidal copper phosphide nanoplatelets with a range of tunable sizes. Detailed mechanistic analysis identifies a prenucleation chemistry that is atypical for aminophosphine-based metal phosphate syntheses but leads to exceptionally high-quality nanocrystals with tunable localized surface plasmon resonances between 1440 and 1750 nm.
Schimpf synthesizes electrically conductive metal-oxide frameworks that use first-row transition metals to bridge \([\text{Na}_5\text{P}_{30}\text{W}_{140}\text{O}_{110}]^{14-}\) clusters.\(^{26}\) Interestingly, the frameworks are isostructural regardless of the identity—or combination of identities—of the bridging ions. Schimpf presents a sophisticated method for synthesis of a series of Ni/Co/Cu-selenide core/tungsten-selenide shell heterostructured nanoparticles.\(^{27}\) This synthesis is accomplished in “one pot” through the use of ligands that control the reactivity of the tungsten precursor, and, in some cases, the cores can be removed to leave hollow tungsten selenide nanocrystals.

**Alexander Spokoyny** from the University of California, Los Angeles, and his group led a large experiment and theory collaboration that introduces boron clusters as terminal oxidants and weakly coordinating anions for molecule-photocatalyzed, visible-light-driven polymerization of styrene and derivatives.\(^{28}\) The molecular weight of the resulting polystyrene is tunable through halide functionalization of the monomer.

Spokoyny also describes methodology for atom-precise synthesis of Au-based nanoclusters with diverse surface chemistries that could be designed as multivalent binding targets for proteins and other biomolecules.\(^{29}\) Further, Spokoyny reports the synthesis of an air-stable, aryl-functionalized Au(III)-aminophosphine complex that serves as a precursor for cysteine S-arylation of a variety of biomolecules, and enables the formation of macromolecular assemblies of these molecules in controlled configurations.\(^{30}\)

We include in this Virtual Issue along with the TableTalks speakers the latest recipients of the ACS Jonathan L. Sessler Award for Emerging Leaders in Bioinorganic and Medicinal Inorganic Chemistry. **Justin Wilson** from Cornell University (2019 recipient) and his group detail a microwave-assisted combinatorial synthesis of 80 rhenium(I) tricarbonyl complexes with potential anticancer activity, and identified three compounds that exhibited useful inhibitory activity with respect to three cancer cell lines.\(^{31}\) Further analysis of the most promising compound suggests that it induces necrosis of cancer cells. Wilson also presents a new size-selection strategy for purifying light lanthanide ions from ion mixtures using aqueous complexation by “macrophosphi,” which have, for example, a binding affinity for La\(^{3+}\) that is a factor of five higher than its affinity for Gd\(^{3+}\).\(^{32}\) Wilson’s work “Radioactive World: An Outreach Activity for Nuclear Chemistry” describes two K-12 activities intended to communicate concepts related to nuclear structure and stability and the difference between radiative and radioactive decay.\(^{33}\)

**Eszter Boros** (2020 recipient) and her group at State University of New York at Stony Brook report a high-throughput method to compare the luminescence quantum yields of lanthanide complexes excited by Cherenkov-radiation. They demonstrate the ease and accuracy of the method for a library of terbium(III) complexes.\(^{34}\) The motivation here is the potential usefulness of lanthanides as biological imaging agents, for which quick, imaging-based screenings of quantum yields are essential.

Boros also reports a new mass spectrometry approach to quantifying the concentrations of coordinated waters within para- and diamagnetic metal complexes, including lanthanide complexes, in the gas phase.\(^{35}\) Adding temperature-dependent measurements allows them to identify complexes with inner-sphere water ligands and to derive thermodynamic parameters for
inner and outer-sphere hydration. Boros applies her method to Ga, Sc, and Zr complexes under active study in the clinic.

Boros further demonstrates the systematic tuning of the biostability and biocompatibility of copper complexes using macrocyclic chelators.\textsuperscript{36} In addition to fundamental structural and electrochemical studies of these compounds, Boros’ group tests confirm the metabolic stability of a five-coordinate compound in vivo using isotope-labeled versions that they appended to a prostate-specific membrane antigen targeting dipeptide.

We want to thank all authors of these Virtual Issue articles for stimulating contributions that highlight the breadth and depth of inorganic chemistry. We also want to thank Ana de Bettencourt-Dias, Alison Butler, and everyone in the DIC leadership team for initiating and organizing the Periodic TableTalks program and helping establish the Sessler Award. In a year when it was hard or impossible to meet and interact with colleagues beyond our own institutions, TableTalks in particular helped us remain engaged and connected as a scientific community and amplified the voices of our community. May the elements remain in style in 2021 and beyond.

Javier Vela, Guest Editor\textsuperscript{1,2}* ORCID: 0000-0001-5124-6893
Emily A. Weiss, Guest Editor\textsuperscript{3}* ORCID: 0000-0001-5834-463X

\textsuperscript{1}Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States.
\textsuperscript{2}Ames Laboratory, Ames, Iowa 50011, United States.
\textsuperscript{3}Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, United States.

Notes
Views expressed in this editorial are those of the authors and not necessarily the views of ACS.

References


Rachkov, A. G.; and Schimpf, A. M. “Colloidal Synthesis of Tunable Copper Phosphide Nanocrystals.” Chem. Mater. 2021, 33, 1394–1406. DOI: 10.1021/acs.chemmater.0c04460


