

Guest Editor Profile

Find out more about this author's research at <https://doi.org/10.1002/ejic.201801499>.

Antonio Romerosa

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In one word, how would you describe your research? Nice.

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Is your current research mainly curiosity-driven (fundamental) or rather applied? Both aspects, curiosity and possible application of the findings, are present: first I am very curious about how molecules react with each other, but also, just further, in their possible application. I am convinced that chemistry is just beautiful, but it is better if it is also useful.

What was your main motivation to go into this area of research? I have liked all topics of chemistry since I was a child: inorganic, organic, theoretical chemistry, etc. When I studied coordination chemistry, I realized that this was the area in which I had to have knowledge, so I decided to focus my professional career in this area of research.

What aspects of your research do you find most exciting? I enjoy it very much when I find something really new. I am very excited when, for example, I obtain a new and strange compound with new and unexpected properties.

What was your most exciting result to date? All the results I have obtained to date have been very exciting to me, but particularly those obtained at the beginning of my career when I got my permanent position at a new University where there was nothing and it was necessary to do everything: to install labs, to find money, to improve the skills of students, etc. The results I obtained in that period are the most valuable in comparison with the poor conditions I had to get them under.

How do you celebrate a successful paper/breakthrough? I communicate the good news immediately to the rest of the authors, and, if possible, we celebrate by having coffee or something similar.

Neutron Scattering in Coordination Chemistry

John A. Stride,^{*[a]} Wendy L. Queen,^{*[b]} and Antonio Romerosa^{*[c]}

Coordination chemistry has been studied for well over 200 years, and today the field is a well-established sub-discipline that links fundamental chemistry to physics, biology, and materials science. Current key areas of study are the design of new coordination complexes and polymers with a range of interesting properties, the study of the metal coordination geometry and their extended solid-state structures, molecular dynamics, and the magnetic properties of both single-ion systems and highly exchange-coupled materials. Coordination compounds include a range of materials, such as metallocenes, metal–organic frameworks, single molecule magnets, and bio-mimics. Considering the structural complexity of such systems, understanding the structure-derived function is of utmost importance. While a variety of spectroscopic, diffraction, microscopy tools etc., have been employed to gain insight into how to design materials with enhanced properties, it is hard to imagine the current state of understanding in all of these areas without the significant contributions made from neutron scattering. While neutrons are perhaps not the most obvious of probes to a coordination chemist, neutrons have been and remain central to the development of the coordination chemistry field, particularly in the last few decades. As such, a review of neutron scattering as a tool in coordination chemistry is a timely one. It is meant not only to demonstrate the important contributions made to the field, but also to help bridge the knowledge gap for new coordination chemists, providing insight into how neutrons can be employed in the field. As such, in this special issue, we have brought together contributions from several researchers who regularly use neutrons to study coordination complexes. This comes at a time at which we sit on the cusp of yet further progress in terms of neutron scattering facilities, with the emergence of high-brilliance third generation neutron sources such as the Spallation Neutron Source at Oak Ridge (USA), the JPARC facility in Ibaraki (Japan), and the European Spallation Source in Lund (Sweden).

Neutron scattering was a core aspect of Associate Professor John A. Stride's Ph.D. thesis (1996) completed at the University of East Anglia (UK). Subsequently, he accepted a postdoctoral fellowship with Ferenc Mezei at the Hahn-Meitner Institute, Berlin (now the Helmholtz-Zentrum), where he worked on developing new concepts in instrumentation focused on long pulse neutron spallation sources. In 1998, he moved to the Laboratoire Léon Brillouin, Saclay, to take up a second postdoctoral fellowship working in collaboration with Olivier Kahn, looking at polarized neutron diffraction of molecular magnetic material. In 2000, he took a scientific position at the Institute Laue-Langevin, Grenoble, and was responsible for the time of flight spectrometer IN4. In 2005 he took up his first university appointment at the University of New South Wales, Sydney, where he has established a research group focused around inorganic chemistry and chemical physics. Key areas of current research are molecular magnets, nanomaterials, and classical molecular dynamics and structure. Much of this research continues to make use of neutron sources, most of his experiments now performed at the Australian Centre for Neutron Scattering, Sydney. A self-confessed neutron-tragic, he aims to enthuse a new generation of chemists to think beyond the bench and benefit from the insights that neutron scattering techniques can bring to their research.



Professor Wendy L. Queen received her Ph.D. from Clemson University (USA) in 2009. Afterwards, she accepted a postdoctoral fellowship from the National Research Council, which was carried out at the NIST Center for Neutron Research (USA). In 2012, she took a scientific position at the Molecular Foundry at Lawrence Berkeley National Laboratory, and in 2015 she accepted an Assistant Professorship in the Institute of Chemical Sciences and Engineering at École Polytechnique Fédérale de Lausanne (EPFL) in Switzerland. Her research is focused on the synthesis and characterization of novel porous adsorbents, namely metal–organic frameworks, that are of interest in a number of host–guest applications. The ultimate goal of her research is to contribute knowledge towards solving globally relevant problems, like reducing energy consumption, cutting CO₂ emissions, and water purification. Her desire is to help train a new generation of researchers that have the knowledge and scientific skill set necessary to become future frontrunners in energy-related research.



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For newcomers to the concept of neutron scattering in coordination chemistry, an excellent introduction is provided in the contribution by Xue et al.,^[1] who give a contemporary review of the techniques available and the types of instrumentation and measurements achievable. They further provide insight into how these techniques can be employed for the advanced characterization of coordination complexes.

The large incoherent neutron cross-section of protons makes inelastic scattering (INS) a supremely sensitive technique to directly probe the dynamics of ligands bound to metal centers. Further, the interaction between neutrons and protons simplifies the process of calculating inelastic neutron scattering (INS) spectra based on the solid-state crystal structure. The direct comparison between model and measurement can provide an understanding of the frequency and spatial extent of molecular deformations. This is beautifully demonstrated in the contribution of Parker et al.^[2] on the sandwich metallocene, ruthenocene, where the complementarity between neutron spectroscopy and optical spectroscopy, such as infrared and Raman, coupled to density functional theory calculations, is evident, leading to a definitive assignment of the vibrational modes.

Neutrons have a magnetic moment making them inherently sensitive to local perturbations of magnetic field or magnetic moments within materials. The first demonstration of antiferromagnetic coupling was via magnetic, neutron diffraction experiments carried out in MnO by Clifford Schull,^[3] who later received the 1994 Nobel Prize in Physics for his contributions to the field of neutron scattering. Since then, the magnetic properties of coordination complexes are often the subject of neutron scattering experiments. A potentially complicating factor, however, is, more often than not, the requirement to replace the hydrogen atoms present in the complex with deuterium (i.e. d-analogues of the parent material) in order to silence the incoherent scattering of protons undergoing vibrational excitations and diffusion. However, in cases where ligands can be readily deuterated, the magnetic signature of coordination compounds can be probed both in terms of structure and dynamics. Within this edition, there are several elegant examples of the application of neutrons to the study of magnetism; Boskovic et al.^[4] provide a review of INS measurements of lanthanoid-based single molecule magnets that includes some discussion of available instruments. Meanwhile the significance of the anisotropic first-row transition metal ion Co(II) as a magnetic center is investigated in the behavior of the classical coordination complex $[\text{Co}(\text{acac})_2(\text{H}_2\text{O})_2]$ as a mononuclear single molecule magnet (SMM).^[5] Further, Carretta et al. demonstrate the impact that Co(II) can have on an otherwise antiferromagnetic $\{\text{Cr}_7\text{Co}\}$ wheel with their investigation of the $\{\text{Cr}_7\text{Co}\}$ SMM using a newly developed tool, 4D-INS, where single crystal data is spliced and cut across both spatial and temporal spin space.^[6] This type of experiment, which can be matched precisely to theoretical models, was truly impossible just a few years ago. The final molecular magnet contribution to this volume is that of Prsa and Waldman, who show the power of spin-wave calculations in the study of Mn-based SMMs, complete with a review of the underlying theory.^[7]

Metal-organic frameworks (MOFs) are a recent addition to the field of coordination chemistry in the last few decades; these



Antonio Romerosa was born in Granada (Spain) in 1964. He graduated in 1987 (University of Granada) and received his PhD (Universitat Autònoma de Barcelona) in January 1992. In the same year he undertook postdoctoral research at the ISSECC CNR (Florence, Italy), now ICCOM CNR, before becoming Lecture Professor (1997) and finally Full Professor (2009) at the University of Almeria (Spain). He is author of more than 150 international refereed papers in Inorganic and Multidisciplinary Chemistry, 4 books, 9 Spanish and international patents, more than 210 presentations at national and international meetings and supervisor of more than 18 PhD theses. He was involved in and responsible for National and International Research Projects supported by CEE, NATO, Spanish and Andalucía Government. His research interests range over homogeneous catalysis and organometallic chemistry in water, phosphorus chemistry, photo-inorganic chemistry, bioinorganic chemistry, and natural stones. The interest to understand how water interacts with metal complexes, which can be used as new active biological compounds, as catalysts in water, new aquo-active materials, etc., led him to be an active researcher in the experimental neutron field. He is currently responsible for the "Research Laboratory on Sustainable Chemistry" that is located in the CIESOL institute (www.ciesol.es) and is director of the "LIDIR laboratory" (www.lidir.es).

have rapidly moved to the forefront of materials research due to their record-breaking internal surface areas and high structural tunability, which promote their potential application in a number of energy-relevant fields. For instance, Queen et al. have used neutron diffraction to investigate the hydrogen adsorption properties of a sodalite-type MOF, using D_2 as the adsorbate.^[8] Clearly effective hydrogen storage will be crucial if we are to move toward a hydrogen-based economy and this study demonstrates the power of neutron techniques for this increasingly important class of compounds. In a similar class of materials, namely a series of Ru-containing metal-organic polymers, Romerosa et al. used in-situ INS and Raman spectroscopy to investigate the polymer conformation and the nature of the water molecules trapped into the structure.^[9] This novel approach to multiplexing data collection across different complimentary techniques in a single experiment perhaps marks a growing demand for understanding materials of increasing complexity. Given advances in experimental tools and computing power, such in-situ, parallel experiments are expected to become more routine.

The intense color of coordination complexes has been the focus of many researchers over time; indeed, the Prussian Blue pigment, which consists of a mixed-valent Fe-CN coordination network, is often regarded as being one of the first recognized coordination compounds. More recently, the role of coordination centers in dyes and, in particular, their applications in dye-sensitized solar cells, have renewed research efforts related to understanding the optical activity of monomeric complexes. Considering that the coordination geometry is inherently linked to the

optical activity, neutron-determined structures that unveil the precise location of hydrogen atoms can play a key role in understanding their properties. In this special edition, Romerosa et al.^[10] provide a comprehensive study of Ru–bipyridine coordination complexes using a range of methods: single crystal X-ray structure determination, electronic spectroscopy, neutron dispersion studies under visible light irradiation, and theoretical calculations. This work highlights yet again just how neutron scattering experiments are incorporated to a research project as an additional technique for the complete characterization and study of chemical systems; it really can no longer be considered as an exotic, rarely used, method.

A great advantage of neutrons is their relatively weak interaction with matter, making them highly penetrating. This means that sample environments that can otherwise be challenging – low temperatures, magnetic fields or high pressures, etc. – can easily be accommodated on neutron beams. Many of the contributions in this edition feature data recorded at temperatures well below those available to most bench-based chemists, opening up the scope for researchers to study molecular magnetism and excitations from true ground state populations. Yamaguchi et al. have measured diffraction data at pressures relevant to geological environments (GPa) to understand the hydration properties of calcium chloride under conditions that are similar to what is found in interfacial zones of continental plates and the mantle, which is central to earthquake and volcanic activity.^[11]

The value of neutron scattering in the study of coordination compounds cannot be overlooked. This compendium of research papers provides but a snapshot of the field. With continued experimental and computational advances, the boundaries of our understanding in coordination compounds will continue to expand.

Finally, we wish to thank sincerely all contributors, who kindly accepted our invitation and submitted their manuscripts to this special issue, and the editorial team of *EurJIC*.

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