How would you define the core objectives of your group’s current Subsulphide and Subselenide Chemistry project?

The Subsulphide and Subselenide Chemistry grant is a small one that has allowed us to investigate a focused project with one major objective, which is to determine whether or not a new oxidation level of sulphur and selenium exists in coordination complexes. I suggested in a paper I wrote in 2010 that an unusually long S–S bond distance in a particular Cu₃S₂ compound could be due to the presence of an S₂³⁻ ion, which was completely unknown at the time. The aim of this project has been to see if we can identify other S₂³⁻ or Se₂³⁻ compounds to define their major characteristics.

Could you explain what is meant by subsulphide and subselenide chemistry?

‘Subsulphide’ and ‘Subselenide’ are the names I picked for the S₂³⁻ and Se₂³⁻ ions, respectively. These are ‘missing links’ in the redox chemistry of these elements. Most people are familiar with the elemental form of sulphur, S₈, in the gas phase, sulphur is a dimer, S₂, just like molecular oxygen. In compounds with metal cations, several anionic forms of sulphur are known, with the most recognised being the disulphide ion, S₂²⁻, as in pyrite (FeS₂), and the sulphide ion, S₂⁻, as in zinc blende (ZnS). In contrast to these minerals, which have extended polymeric structures in the solid state, molecular compounds have been found that contain not only disulphide and sulphide ligands, but also ‘supersulphide’, or S₂⁻. Until our work, the S₂³⁻ ion, or subsulphide, had been missing. We actually think it has existed for some time but has been overlooked.

What are your findings so far?

We have recently published a paper that reports reinvestigation of a known Ni₂Se₂ compound showing that it contains the Se₂³⁻ ion. As the title of our project implies, we are also interested in exploring the chemical reactivity of the Se₂³⁻ ion. Our first paper therefore describes how the Se₂³⁻ ion can be oxidised forming a product containing the Se₂²⁻ ion. The sulphur compound behaves analogously. This is an interesting result because changing the S oxidation state actually changes the nature of the S–S bond. In this case, we have taken a compound with an S–S half-bond and oxidised it to create a full bond between the S atoms.

What do you consider to be the greatest discovery at the University of Wisconsin-Madison since the Chemistry Department’s establishment?

When I think of the impact of research in the UW-Madison Chemistry Department, it is easy to be overwhelmed. I have tremendous colleagues that continually discover new and exciting phenomena. Picking one discovery in the entire history of our Department is hard to do, although I think that the work of Irv Shain, former Faculty Member, Department Chair and University Chancellor, outlining the theoretical basis for cyclic voltammetry is one of the most lasting contributions.

Aside from Subsulphide, what are the other interests of your research group?

There are two major research efforts in my group that are unrelated to the subsulphide project. In one, we have been capitalising on a synthetic method we have developed to access heterometallic compounds having metal-metal multiple bonds. The idea has been to hold two different metal atoms in close proximity to each other and to see how they affect each other’s electronic structure and reactivity. We are also studying metal-metal bonded compounds that are relevant to catalytic C–H functionalisation reactions. These reactions potentially allow swift access to complicated organic molecules made from very simple starting materials. Our interest is in discovering how the electronic structure of the catalysts affects their reactivity and selectivity for differing C–H bonds in a molecule. One interesting opportunity that we have become involved with is the National Science Foundation’s Center for Stereoselective C–H Functionalisation, which is a major collaborative effort involving over 20 faculty members at many universities. The overall goal of the Center is to revolutionise synthetic organic chemistry by discovering the breadth of C–H functionalisation methodology. Our involvement in the Center is very exciting for me. It will allow researchers all over the US to test new metal complexes that we synthesise in my group as catalysts for a broad range of C–H functionalisation reactions.
Novel concepts in chemical bonding

The research group of Associate Professor John F Berry at the University of Wisconsin-Madison is breaking new ground in sulphur and selenium chemistry, proposing the first half-bonded diatomic ions of these elements.

Deepening the body of knowledge about the chemical composition and properties of substances is essential to understanding the world around us. One discipline that is of particular importance to this is inorganic chemistry, which focuses on the chemistry of elements that span the entire periodic table. To help improve our understanding of transition metal containing compounds, a group of chemists at the University of Wisconsin-Madison led by Professor John F Berry is investigating their chemical and physical properties using synthetic methods, X-ray crystallography, cutting edge spectroscopic techniques, and computational chemistry. The Berry group targets the synthesis of new kinds of transition metal compounds featuring unusual bonding characteristics. Some key areas of study include the metal-metal interactions in paramagnetic heterometallic compounds, reactive catalytic intermediates that have metal-to-metal-to-ligand multiple bonds in a linear structure, and examining whether a new reduced state of sulphur and heavier congeneric selenium and tellurium elements can be stabilised in transition metal complexes. This last topic of research has recently captured their interest.

Identifying new sets of compounds
Bond formation and cleavage are critical to the study of chemistry because bonds are what hold molecules together. The Berry group’s work on proposed half-bonds in a new class of compounds that they call ‘subsulphide’ and ‘subselene’ compounds has been funded for the last two years by the US National Science Foundation’s Chemical Synthesis programme. In common sulphur-containing materials, the sulphur atoms are most typically found in the doubly-reduced mononuclear dianionic ‘sulphide’ form, S\(^{2-}\), or a binuclear dianion, ‘disulphide’, with a sulphur-sulphur bond, S\(^{2+}\). The aim of this research is to test Berry’s proposed hypothesis that a new reduced state of sulphur, i.e. S\(^{2+}\) or subsulphide, can actually be stabilised through coordination to transition metals. Berry describes how his team of chemists and their collaborators have used a number of different physical methods to study the electronic structure of transition metal/sulphur compounds: “We have been researching the electrochemical and chemical reactivity of coordinated sulphur species so that we can clarify the electronic and chemical properties of the subsulphide ion”.

The presence of the new reduced subsulphide state of sulphur suggests that sulphur-sulphur bonds are created and broken one electron at a time, contrary to the conventional two-electron theory. The subsulphide state also suggests the existence of a formal half-bond between the two sulphur atoms. These conclusions would also apply to the heavier elements that are related to sulphur in the chalcogen family, namely, selenium (Se) and tellurium (Te). Berry’s team is investigating a set of unusual compounds first identified and extensively characterised by Sitzmann in Germany in 2001. Although the nature of the chalcogen-chalcogen bonds in these compounds was not understood at that time, investigations by Berry’s team now suggest that these compounds may well include S\(^{2+}\), Se\(^{2+}\) and Te\(^{2+}\) ligands. Operational tests using Se K-edge X-ray absorption spectroscopy, in collaboration with Professor Serena DeBeer and Dr Kyle Lancaster at Cornell University, have yielded convincing results. In this method, X-rays are used to excite core electrons in the Se atoms, and the energy of these excitations is directly
By working on fundamental problems in chemical bonding and electronic structure, Berry's group rationalises the unique physical properties within a number of important systems related to the charge of these atoms. “We saw a linear correlation between the Se K-edge energy and the apparent Se oxidation state that placed the charge of the Se atoms in the Sitzmann compound at –1.49, very close to the ideal value of –1.5 expected for the Se²⁻ ion,” explains Berry. The researchers are now bringing their studies on the sulphur and tellurium compounds to a close, but are confident that their data indicates similarities with the Se compound.

EMPLOYING A RANGE OF CUTTING-EDGE METHODS

Besides X-ray absorption spectroscopy, the researchers also use X-ray crystallography because it can help to pinpoint compounds that have S–S bond distances suggestive of half-bonds. In addition, X-ray photoelectron spectroscopy has proven to be useful to identify specific oxidation states within the compounds. “In work that is not yet published, we have made use of X-ray photoelectron spectroscopy to nail down the physical oxidation states of the Ni atoms in the Sitzmann compounds,” observes Berry. Furthermore, resonance Raman spectroscopy is a useful probe to estimate the strength of the S–S bond by measurement of the energy of its stretching vibration. The observed S–S vibration is much lower in energy than those seen in singly-bonded disulphide compounds, which from Berry’s perspective is quite definitive: “We can easily identify which transition corresponds to the S–S vibration by doing an isotopic substitution of ³⁴S for ³²S,” he reveals.

THE BENEFITS OF ADVANCEMENTS IN TECHNOLOGY

Berry particularly enjoys new investigations that help to elucidate bonding phenomena. By working on fundamental problems in chemical bonding and electronic structure, his group rationalises the unique physical properties within a number of important systems. Another of Berry’s interests is working with students to help understand chemical reactivity within the context of electronic structure. This has the potential to unlock many of the secrets about how chemicals interact, and is of particular importance in the area of catalysis. Using modern computational methods has proven to be especially important for his group’s research and has allowed his co-workers to gain meaningful quantitative comprehension of electronic structure. Rapid progress in technology has important repercussions for science and research. It is Berry’s opinion that the most significant development in technology that has specifically benefited his group has been the increase in the power of computers and computational methods: “Now we can carry out high-level computational studies on compounds that were literally impossible to study before,” he notes. “Consequently, it is now possible to perform calculations on relatively complex molecules on a simple laptop rather than on a supercomputer.”

JOHN BERRY attended Virginia Tech from 1996–2000 where he studied music theory and composition, as well as chemistry. He then worked as an NSF Graduate Research Fellow at Texas A&M University from 2000–4 with F Albert Cotton. From 2004–6, he worked with Karl Wieghardt at the Max Planck Institute for Bioinorganic Chemistry in Mulheim an der Ruhr, Germany. Since 2006, Berry has been an Assistant Professor at the University of Wisconsin-Madison, where he investigates fundamental problems in coordination chemistry and bonding. Berry still writes music in his spare time, and sometimes has occasion to perform on the violin, viola or piano.

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