Ag(II)SO₄: Mr. Hyde of the transition metal sulfates.

With copper(II) sulfate known for millennia, and gold(II) sulfate synthesized a decade ago, silver(II) sulfate was the last coinage metal sulfate awaiting discovery. Now, finally, Ag(II)SO₄ has been synthesized by a team of Polish and Slovenian researchers.

The properties of chemical elements are largely governed by their position in the periodic table: it is the every-day experience of chemists that elements from the same group of the periodic table show very similar properties. But not the coinage metals. Copper, silver and gold differ in their physical properties, colour and chemical reactivity (Fig.1). Marked differences persist also for the chemical compounds of these elements in various oxidation states ranging from −1 to +5. Of particular interest is the divalent (+2) state, which predominates in the chemistry of copper, and is incredibly rare for gold. With an altogether different character, Ag²⁺ is an enormously powerful oxidizer, capable of destroying the majority of simple anionic ligands and is why the chemistry of Ag²⁺ is essentially limited to connections with fluorine and oxygen.

Copper(II) sulfate is found in nature in five different forms, from heptahydrate, through pentahydrate, trihydrated and monohydrate, to an anhydrous compound (Fig.2). The ancient Egyptians used it for dyeing while the ancient Greeks treated pulmonary diseases with it. In modern times it is widely utilized in agriculture for its fungicidal, herbicidal and pesticidal properties, in medicine to test blood for anemia. The ocean blue CuSO₄ x 5 H₂O is probably the best known substance in chemical education sets, owing its fame to the ease of growing large high-quality single crystals. Thus, it was remarkable that AgSO₄ with its ‘textbook’ formula had not been synthesized, especially as that of the heaviest homologue, AuSO₄, had been achieved nearly a decade ago.

Now the team of scientists led by Dr Wojciech Grochala from the University of Warsaw and joined by colleagues from Jagiellonian University of Cracow, Jožef Stefan Institute, IMFM and University of Ljubljana, has managed to synthesize and meticulously characterize AgSO₄. They report two distinct synthetic pathways towards this compound, a ligand-exchange (methathetic) and a displacement reaction route. Speaking of their results, Dr Mariana Derzsi, a theoretician in the team, said “Actually, we were not surprised to find that AgSO₄ is a genuine sulfate (VI) of divalent silver, and neither a mixed valence Ag(I)/Ag(III) compound nor the peroxodisulfate of Ag(I). Our team predicted
the properties of this fascinating compound from first principles and all our theoretical results pointed in its favor.”

AgSO₄ contains Ag²⁺ cations in the homolectic environment of four sulfate anions; each anion utilizes all four oxygen atoms for bonding to silver, thus linking cations with one another into a 3D network. “But the crystallographic unit cell of AgSO₄ is entirely different from those of its Cu and Au analogues” confirm Prof. Wiesław Łasocha and Dr Bartłomiej Gaweł, who contributed to solving of its crystal structure. The compound is deep black (Fig.3), unlike any other known sulfate of a transition metal. It also exhibits a range of anomalous properties, such as a very narrow electronic band gap of less than a quarter eV, and the presence of a low–energy electronic charge–transfer transition. “This weird inorganic compound is really different to any other sulfate you could think of” says Dr Zoran Mazej, who carried out syntheses utilizing the methathetic pathway. “The presence of Ag(II), an aggressive oxidizer, is responsible for that” he adds.

And when he says ‘aggressive’ he really means it. As initial tests show, AgSO₄ would oxidize the majority of unsaturated and even aromatic organic compounds. “CuSO₄ is as innocent as Dr Jekyll when compared to AgSO₄, which is a real Mr Hyde (Fig.4)” says Mr Przemysław Malinowski, the PhD student who synthesized very pure AgSO₄ using the displacement route.

But most fascinating of all are the magnetic properties of the new compound. There is a substantial spin density on the oxygen atoms, which results in an unexpectedly strong antiferromagnetic exchange. “It is unusual that antiferromagnetism persists up to nearly 400 K, the temperature at which AgSO₄ thermally decomposes” says Dr Zvonko Jagličić, responsible for performing magnetic measurements. “All other known sulfates order magnetically at temperatures ten times lower” he adds. The implication is that AgSO₄ could be used as a precursor to a high–temperature superconductor. Commenting on how this could be achieved, Dr Wojciech Grochala said, “The great challenge now is to chemically dope this compound, use external pressure to close its electronic band gap, and let high–frequency S–O stretching vibrations finish the job for us”. He added, “Despite various technical difficulties I am really excited about the prospect”.

The results will be published in a forthcoming issue of the prestigious journal, Angewandte Chemie, but is available as a VIP (Very Important Paper) on the internet now. The work is dedicated to Jan Czochralski, eminent Polish chemist.