

Under sulfur's spell

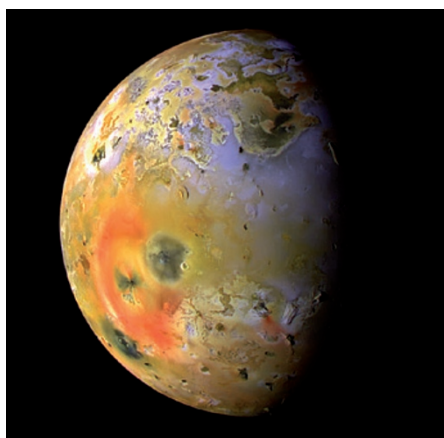
Thomas Rauchfuss marvels at the diversity of sulfur reactivity. Although it poisons most industrial catalysts, it adopts many forms in nature and takes on a variety of biological roles — including that of a biocatalyst.

What is sulfur? This is a tricky question, because many species with the formula S_x are known. The most stable at room temperature is the crown-shaped ring S_8 , but elemental sulfur also contains small amounts of the bright-yellow S_2 , and tiny amounts of other rings. On heating, sulfur readily converts to a metastable one-dimensional elastomer, which quickly degrades at room temperature back to the S_8 form. The tendency of sulfur to form rings and chains (to catenate) is its most distinctive property. Only at high temperatures does sulfur form S_2 , the analogue of O_2 .

The catenating tendencies of sulfur are also evident in its anions — the polysulfides with formula S_x^{2-} . They arise by simply adding small amounts of reducing agents to elemental sulfur. These chains of sulfur atoms, which resemble alkanes in their conformation, can be extended or further shortened by redox reactions, a process that is exploited in the sodium–sulfur battery. The anionic chains exist in dynamic equilibrium with radicals such as $S_3^{\cdot-}$ — the blue chromophore in lapis lazuli. The anions that terminate these chains can be capped with alkylating agents, protons and metal cations¹. With metals, one obtains compounds with such improbable formulae as PtS_{15}^{2-} and $Fe_2S_{12}^{2-}$.

Sulfur is readily oxidized, notably to dioxide and trioxide species. Depending on their environment, microorganisms subsist on the hydrolysed derivatives of these oxides through anaerobic respiration. Sulfur dioxide, an electrophilic, bent analogue of carbon dioxide, is produced on a massive, even weather-changing, scale by volcanic eruptions. Further oxidation gives the trioxide precursor to sulfuric acid, produced annually on the scale of about 140 megatons.

Sulfur is featured in two coded amino acids, methionine, which is fairly boring to the sulfur chemist, and cysteine, which has spectacularly diverse roles. By forming S–S bonds, the conversion of cysteine to



Io, a moon of Jupiter, has diverse colours owing to the presence of various sulfur species.

cystine rigidifies proteins in a manner similar to the crosslinking provided by the S–S bonds in vulcanized rubber. Otherwise, the thiol group is a favoured site for post-transcriptional modifications. Sulfur is featured in many cofactors and vitamins, for example, thiamine, biotin and lipoic acid. Elucidation of their biosyntheses has been a trove of novel mechanisms.

As sulfur has occurred in proteins for millennia, fossil fuels often contain a few per cent by weight of organosulfur compounds, most problematically in the form of thiophenes. A continuing focus in petroleum refining is the removal of this sulfur, especially in view of the 5 ppm allowed limit of sulfur in many diesel fuels. This technology, called hydro-desulfurization, relies on modified molybdenum sulfide catalysts to yield a low-sulfur product and hydrogen sulfide waste. Oxidation of the waste produces vast amounts of sulfur, which beckons for new applications.

Thiolates exhibit particular affinity for metal ions; in enzyme active sites metals are commonly anchored via cysteinyl residues. The resilience of the metal–thiolate bond is exploited in the role of thiols in the formation of self-assembled monolayers. These materials are formed by simply contacting thiols with

gold surfaces. Self-assembled monolayers are crucial in nanotechnology because they provide a responsive interface between mobile phases (gases and liquids) and an electrically conductive device.

The role of metal–sulfur bonds in biocatalysis is a popular area of research. One of the challenges is to elucidate the mechanism of methanogenesis — the source of the majority of Earth's natural gas and a contributor to climate change. The final stage of methanogenesis involves scission of a methyl–sulfur bond in coenzyme-M (first isolated from the sewers of Urbana, my home town). The allure of this area is heightened by the discovery that methanogenesis can run in reverse, through a nickel-catalysed reaction of methane².

Transformations relevant to 'bioenergy' are effected by Fe–S clusters, including the conversions of CO_2 to CO, of protons to H_2 , and of N_2 to NH_3 (ref. 3). These processes all involve the coordinated movement of protons and electrons — a mechanistic theme of immense significance. The active sites of the relevant enzymes consist of metal clusters where sulfide ligands help 'glue' together the metals. Because changes in electron count barely affect their structures, metal–sulfide clusters are able to quickly accept and relay electrons, as required for efficient catalysis. Apparently the presence of the soft sulfur ligands also enables the metal centres in these catalysts to bind and thereby activate weakly basic substrates such as H_2 , CO_2 and N_2 — ligands normally reserved for organometallic compounds. Our ability to master these transformations could be key to our future. □

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References

1. Devillanova, F. A. (ed.) *Handbook of Chalcogen Chemistry: New Perspectives in Sulfur, Selenium and Tellurium* (Royal Society of Chemistry, 2006).
2. Thauer, R. K. *Angew. Chem. Int. Ed.* **49**, 6712–6713 (2010).
3. Fontecilla-Camps, J. C., Amara, P., Cavazza, C., Nicolet, Y. & Volbeda, A. *Nature* **460**, 814–822 (2009).

