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Essay

Copper Curiosity: From Blue Blood to Click Chemistry

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The Copper Age dates back around 5000 years and describes the early Bronze Age when copper was still used in its pure form rather than as an alloy with tin, better known as bronze.[1] The contemporary name of copper comes from Roman times when the metal was called 'cuprium', named after Cyprus where it was mined. Cuprium was later simplified to 'cuprum' and ended up as 'copper' in contemporary English.

The popularity of metallic copper is related to its relatively easy isolation from various ores, its wide availability as the 26th most abundant element on Earth, as well as its being rather insensitive to air and water. During the Roman and Greek periods, copper was used to make a wide range of objects such as cutlery, statues, and coins. Based on the high thermal conductivity of copper, it was also a popular material for making kettles and pans. Nowadays, copper is still an important metal and can be found in plumbing as pipelines for water. The first evidence of copper being used in water plumbing comes from ancient Egypt. Copper tubing used for the supply of water for purification rituals in temples and pyramids has been found to be still in good working condition after around 5000 years.[2] The main present use of copper is in electrical devices as copper is the second best electrical conductor after the less abundant and more expensive silver. As such, copper is extensively used in, for example, electrical wiring as well as electrical contacts.

Nowadays, copper roofing is considered as artwork for buildings because of the beautiful green colour that appears upon oxidation of the upper layer into verdigris, mainly consisting of copper(II) acetate. Importantly, the formation of this thin oxidation layer protects the bulk copper from further oxidation in stark contrast to iron, which has led to the popularity of copper roofing in the first place. The production of larger amounts of verdigris pigments was done in Roman times by hanging a thin plate of copper over a bath of vinegar to quickly obtain copper(II) acetate.[3] Such verdigris pigments have been utilized by famous painters, including the Flemish painter Jan van Eyck.

This latter example of the formation of an oxidized copper pigment layer on roofing links metallic copper to the stable copper(I) and copper(II) oxidation states. These stable copper ions are essential nutrients for living matter, although they are also used in agrichemical pesticides. Solutions of copper(II) salts act as fungicides and prevent the formation of algae. However, the human liver can efficiently excrete copper ions from the body, making it relatively invulnerable to copper. On the contrary, copper ions are essential for human life because they are located in the catalytic site of various enzymes, including galactose oxidase and tyrosinase. A particularly appealing occurrence of copper ions in living matter is the protein hemocyanin that is present in the blood of, amongst others, octopuses and horseshoe crabs. Hemocyanin is the copper analogue of the human iron containing protein hemoglobin and accounts for the uptake and transport of oxygen. Hemocyanin contains two copper(I) ions in the absence of oxygen, which are oxidized into copper(II) upon oxygen binding, giving rise to a strong blue colour.[3] As such, these animals truly have 'blue blood', which is the term often used to refer to nobility.

In the last decades, sophisticated copper catalysis has led to the establishment of two major advancements in chemical sciences, namely atom transfer radical polymerization and click chemistry. Atom transfer radical polymerization was one of the first developed methods to gain control over free radical polymerizations, allowing precision polymer synthesis based on copper redox chemistry.[4] Copper(I) halide abstracts a halogen from an alkyl halide, leading to a radical together with copper(II) dihalide. This free radical reacts with the monomer until it is transformed back into the alkyl halide by the reverse reaction with copper(II) dihalide. This copper redox equilibrium lowers the concentration of free radicals leading to suppression of undesired termination reactions that scale with the square of radical concentration, while propagation only scales with the radical concentration. The second major concept that was established in the last decade based on copper catalysis is the so-called 'click chemistry' which refers to the most powerful, efficient, and clean coupling reactions that occur under mild conditions.[5] The first, and to date still the most popular, click reaction is the copper(I) catalyzed azide-alkyne cycloaddition. Copper(I) is crucial for this reaction to be a click reaction as it highly accelerates the original Huisgen azide-alkyne cycloaddition, making it feasible at room temperature, and it introduces stereospecificity.

Following the rich history of copper utilization by mankind, it is expected that copper will remain one of the most important elements in the future, not only for electrical devices but also for the development of more sustainable chemical syntheses based on copper catalysis.

Conflicts of Interest

The author declares no conflicts of interest.

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