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Chemical Education

A CHIMIA Column

Topics for Teaching: Chemistry in Nature

Turning on a Chameleon Using Nanocrystals of Biogenic Guanine[a]

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Abstract: Dramatic colours and pattern changes in chameleons arise from the optical properties of biogenic guanine nanocrystals.

Keywords: Chameleon redox reaction · Chemical education · Nanocrystals in chameleons

In the previous article in this series of 'Chemistry in Nature' Education Columns, I described the redox chemistry underlying the colour change from yellow to red of some male dragonflies as they mature.[1] Earlier in this series, I introduced the concept of structural colour, exemplified by the violet colour of male purple emperor butterflies; this phenomenon is caused by the interaction of incident lightwaves with the complex structural order at the nano- and microscale present in the butterfly wing scales. The violet iridescence of the butterfly's wings is angle-dependent, and the colour alters when the wings are viewed from different angles.[2] Perhaps the chameleon is the most cited example of an animal that can change its colour. This is so well known that the word 'chameleon' has entered the English language with broad usage. Chamber's dictionary has the following definitions: (i) "slow-moving lizard, found mainly in Africa, whose granular skin changes colour rapidly in response to changes in its environment, acting as camouflage and as a means of communication with rivals"; (ii) "someone who readily adapts to any new environment"; (iii) "a changeable, unreliable person." Throughout his long career, the many personas adopted by David Bowie led to his being described as the "chameleon of pop".[3] In the Middle Ages, chameleons were thought not to eat, but only to live on air, as documented by William Shakespeare in Hamlet "Excellent, i' faith, of the chameleon's dish. I eat the air, promise-crammed. You cannot feed capons so."

The so-called 'chemical chameleon' or 'chameleon redox reaction' is a popular classroom demonstration based upon the colours of different oxidation states of manganese, and a teaching-notes sheet describing one approach to the experiment can be downloaded from the Royal Society of Chemistry.[4] The reaction involves reduction of a purple solution containing $[MnO_4]^-$ to produce green $[MnO_4]^{2-}$. Further reduction leads to the precipitation of MnO_2 which, at the concentrations used in the experiment, appears as an orange colloid rather than a brown precipitate.

The changing colours of a chameleon have captivated scientists for centuries, and in 1968, A. E. Best[5] stated: "There are few occurrences more apt to arouse curiosity. Yet until the nineteenth century the study of this phenomenon was a forlorn attempt to find laws in a situation too complex for controlled observation." Best provides a fascinating historical account of the varying explanations put forward over time to account for the changes in colour. At the time of publication in 1968,[5] the favoured explanation (now proven incorrect) involved the movement of different coloured pigments in a chameleon's skin cells. Although it is often stated that chameleons change their skin colour to match their background, this is incorrect. Figs. 1 and 2 both illustrate the flap-necked chameleon (*Chamaeleo dilepis*), which is widespread in southern Africa in areas of savannah and bushveld. Both photographs in Figs. 1 and 2 were taken at the same time of year: one at night when the animal was resting or asleep (Fig. 1) and one during the day when the chameleon was crossing a dirt road (Fig. 2). The slow movement of chameleons makes them very vulnerable to predators when they are out in the open. The colour difference and skin patterning between the chameleons in the two photographs are remarkable and illustrate not intentional camouflage (even though the photographs might suggest this), but mood. For example, a male chameleon rapidly changes colour when it is confronted by a rival male.

Fig. 1. A relaxed flap-necked chameleon (*Chamaeleo dilepis*) at night. Photo credit: Edwin Constable.

Fig. 2. A flap-necked chameleon on the move and exposed to danger. Photo credit: Edwin Constable.

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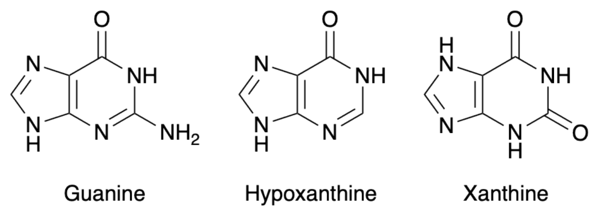
Definition: A nanocrystal is a crystal with dimensions in the nanometre regime, often, but not exclusively, restricted to those with one dimension ≤100 nm.

Guanine (Scheme 1) is a nucleotide base, and is one of the building blocks of RNA and DNA. However, guanine has another important role in biology. Crystals of guanine are highly reflective and are commonly associated with structural colour and visual systems in animals. The optical property of guanine originates from a high refractive index (n = 1.83). Before proceeding, we need to distinguish between cells called *chromatophores* that contain coloured pigments, and those called *iridophores* that are the origin of structural colour. Guanine nanocrystals are often present in iridophores and are responsible for producing reflected light of varying wavelengths. The wide variation in colour patterns in, for example, lizards, is achieved through a combination of chromatophores and iridophores.[6] In 2015, a team from the University of Geneva demonstrated that the panther chameleon (*Furcifer pardalis*) changes colour by altering the arrangement of a lattice of transparent guanine nanocrystals present in the upper layer of its skin.[7] Chameleons contain two thick layers of iridophores, with different but specific functions; chromatophores are also present and are responsible for the skin's base colour in the animal's resting state. The iridophores in the lower (deeper) layer contain non-ordered guanine crystals with dimensions in the range 90–600 nm. These reflect infrared radiation, suggesting a role in keeping the animals cool in strong sunlight. In contrast, the upper layer of iridophores contains a different type of guanine crystal with a diameter of 127±18 nm. When these guanine crystals are closely spaced, the iridophores reflect short wavelength light at the blue/green-end of the visible spectrum. This is the condition of a chameleon in a relaxed state. Reorganization of the nanocrystals so that the spacings are larger results in the reflected light having a longer wavelength, giving rise to red, orange or yellow colours seen by the eye.



Scheme 1. Structures of guanine, hypoxanthine and xanthine. In the gas-phase, the 9H and 7H tautomers are of similar stability.[8]

Guanine crystals and nanocrystals can exhibit multiple morphologies, including plate-like crystals, prisms and block-shaped crystals. These are associated with structural colour in nature, and their occurrence varies significantly from one animal to another. In 2022, Palmer and coworkers[9] showed that the guanine crystals and nanocrystals found in nature are not pure guanine, but co-crystals containing predominantly guanine and hypoxanthine, and occasionally xanthine (Scheme 1). To consider the structure of this so-called biogenic guanine, we start with the β-guanine polymorph, containing the 7H tautomer, shown in Fig. 3. The molecules exhibit intermolecular hydrogen bonding and are arranged in sheets. With β-guanine crystals acting as the host material, up to 20 mol % of hypoxanthine (the guest material) can be accommodated in the crystal lattice. This means that some molecules of guanine in the host lattice are replaced by molecules of hypoxanthine. Consider the circled molecule in Fig. 3; replacing this by a hypoxanthine molecule effectively replaces the C–NH_2 unit at the bottom of the circled molecule in Fig. 3 by a C–H unit and causes little disruption to the overall solid-state structure. Interestingly, however, there appears to be no correlation between crystal morphology and the amount of guest compound incorporated, and optical properties are little affected. Palmer and coworkers[9] state that: "It seems that organisms 'make use of what they have', building their crystals from mixtures of structurally similar purines available from nitrogen metabolism."

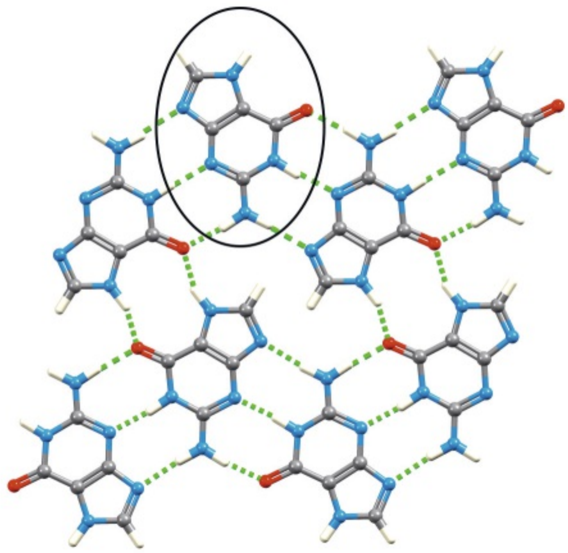


Fig. 3. Part of one hydrogen-bonded sheet in the single crystal structure of β-guanine. Hydrogen bonds (N–H...N and C=O...H–N) are shown in green hashed lines. See text for an explanation of the circled molecule. (The structure was drawn using coordinates from the Cambridge Structural Database and with the program Mercury CSD v. 2022.3.0;[10] CSD structure refcode KEMDOW01.[11])

The word 'chameleon' is synonymous with 'change', notably colour change. This article has described how the chameleon uses the optical properties of biogenic guanine crystals and nanocrystals to effect dramatic colour changes. The different aspects discussed provide a unique example of the interplay of chemistry, biology and physics in understanding an unusual and impressive facet of the natural world.

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[a]This column is one of a series designed to attract teachers to topics that link chemistry to Nature and stimulate students by seeing real-life applications of the subject.