THE ELECTRON DIFFRACTION COMPANY

Biogenic crystal structure determination with 3D ED.

Guanine solved directly from crude biological material – spider integument, fish scales and scallop eyes.

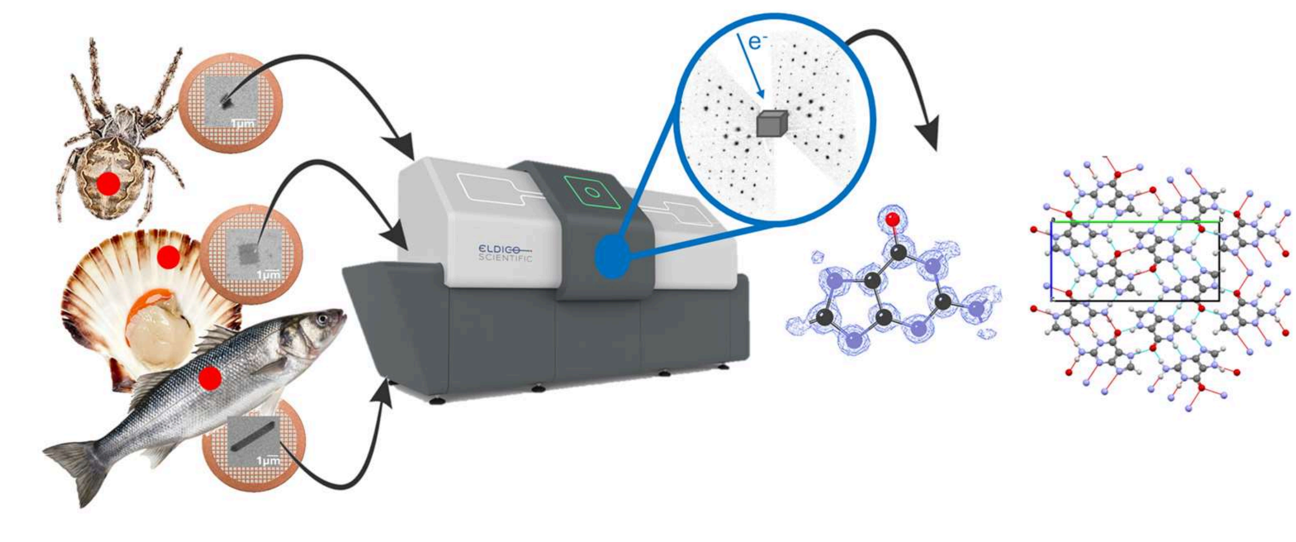

Fig. 1 Biogenic guanine crystals from spider integument, scallop eyes and fish scales, measured on the ELDICO ED-1: electron diffraction yields an electrostatic-potential map and, from it, the β-guanine crystal structure.

Biogenic crystals are naturally occurring crystalline materials produced by living organisms. Examples include calcium oxalate crystals in plant tissues, magnetite crystals in certain bacteria and animals, and various biominerals found in the human body. Their fundamental role in biological processes makes them a subject of great scientific interest, but their complexity and sensitivity present significant challenges for analysis and characterisation.

The susceptibility to undergo damage upon extraction from the parent organism presents major challenges to structure determination of biogenic molecular crystals. The size range spanning from nanometers to micrometers and the limited quantities make it very difficult to determine their structures using traditional methods such as single-crystal X-ray diffraction (SC-XRD) or powder X-ray diffraction (PXRD).

Electron diffraction

3D electron diffraction (3D ED) methods, also known as microcrystal electron diffraction (microED), have experienced rapid advancement in recent years. Although conceptually akin to SC-XRD, 3D ED offers a distinct advantage by using electrons for the diffraction experiment. Thanks to the strong interaction between electrons and matter, 3D ED data can be collected from crystals with volumes 10^6 times smaller than those required for X-ray diffraction, even when coexisting in a mixture. Thus, crystals that traditionally would have been considered powder samples by X-ray standards can now be handled as single crystals by electron diffraction.

ELDICO ED-1

The ELDICO ED-1, the world's first dedicated electron diffractometer, was built to measure crystallites in the nanometer range under ambient or cryogenic conditions. It is designed to collect data with a minimal electron exposure of <0.01 $e^{-}Å^{-2}s^{-1}$, illuminating only the area of interest during data collection in both imaging and diffraction mode. This makes it optimal for data collection from beam-sensitive materials such as organic crystals.

Read the paper: A. Wagner, J. Merkelbach, L. Samperisi, N. Pinsk, B. M. Kariuki, C. E. Hughes, K. D. M. Harris, B. A. Palmer, *Cryst. Growth Des.* 2024, 24, 899–905.

CASE STUDY

Guanine in spider, fish & scallop.

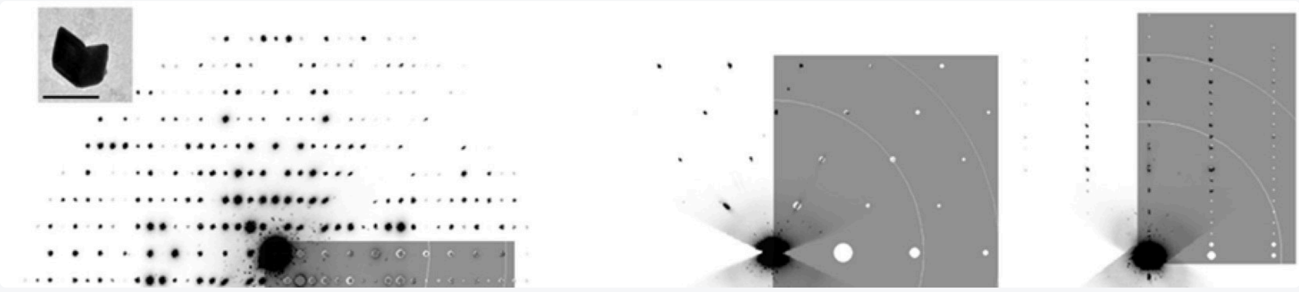

Fig. 2 With the ELDICO ED-1, the experimental diffraction data (left) show a perfect match with the simulated data (right).

Β-GUANINE REFINEMENT – FISH / SPIDER / SCALLOP

Resolution (Å)	**0.67 / 0.67 / 0.80**
Reflections	**5155 / 6019 / 2289**
Completeness (%)	**87.4 / 97.7 / 80.2**
R1 (all refl.)	**0.195 / 0.278 / 0.446**
R1 [I>2σ]	**0.177 / 0.241 / 0.374**
wR2 (all refl.)	**0.537 / 0.540 / 0.735**
Goodness-of-fit	**2.43 / 2.03 / 3.01**

In collaboration with scientists from Ben-Gurion University of the Negev, Cardiff University and the ELDICO application team, we analysed biogenic guanine crystals extracted from fish scales, spider integument and scallop eyes.

The β-polymorph of guanine was refined for all three sources (see table). Crucially, the hydrogen atoms were located directly in our structure determinations from 3D ED data, representing an improvement in the quality of the β-guanine crystal structure compared with the structure published previously.

Conclusion. The findings represent a crucial step forward in understanding and harnessing the potential of biogenic crystals for sustainable and bio-compatible optical applications. Key benefits of the ELDICO ED-1 here: effortless data collection; ab-initio structure solution; refinement of the structures free from restraints; no need for a pure compound, with data collected directly from crude material; and accurate electrostatic-potential maps from which hydrogen atoms could be located directly.

[1] A. Hirsch, D. Gur, I. Polishchuk, D. Levy, B. Pokroy, A. J. Cruz-Cabeza, L. Addadi, L. Kronik, L. Leiserowitz, *Chem. Mater.* 2015, 27, 8289–8297.