

Herapathite

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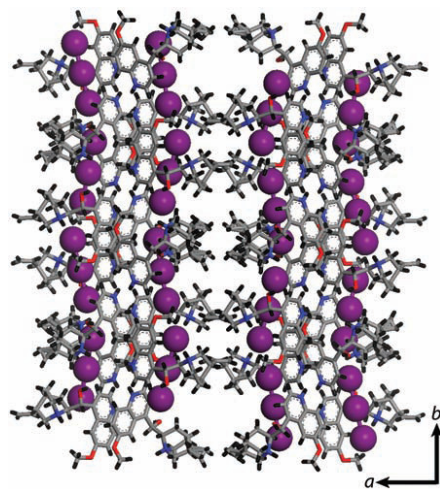
Few crystalline substances are as celebrated in the history of optics as is herapathite, first prepared when an assistant to the toxicologist William Bird Herapath precipitated-metallicreflecting, needle-shaped crystals upon dropping tincture of iodine into the urine of a dog that had been fed quinine (1). Herapath reported that, when the transparent crystals sat one upon the other at right angles, the overlap was “black as midnight.” He recognized that his crystals functioned as excellent linear light polarizers absorbing virtually all the light polarized along the shorter axis of the best-developed face [supporting online material (SOM) text] (fig. S4) and declared that “there is no doubt” herapathite, the name coined by Haidinger (2), will soon replace costly tourmaline polarizers and Nichol prisms (3). Sir David Brewster wished for crystals large enough to add special effects to his invention, the kaleidoscope (4). Herapathite captured the attention of Stokes; he analyzed its remarkable reflectivity (5, 6). Applications of herapathite were not forthcoming for 75 years when Land oriented fragile microcrystals of herapathite in extruded polymers, a process that produced the first large-aperture light polarizers (7, 8) and launched the Polaroid empire. Curiously, despite the widespread use of herapathite polarizers in goggles, as photographic filters, and for stereoscopic imaging, as well as their role as the progenitors of the many polarizing plastics prepared subsequently, the structure of herapathite has never been established.

The composition of Herapath's salt was established by Jørgensen as $4\text{QH}_2^{2+} \cdot 3\text{SO}_4^{2-} \cdot 2\text{I}_3^- \cdot 6\text{H}_2\text{O}$, where Q is quinine, $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$ (9, 10). In 1896, herapathite was used to study x-rays rather than vice versa as in this study. Just 7 months after the discovery of a new kind of radiation by Röntgen, Mayer (11) failed to polarize x-rays with herapathite. West (12) established that the herapathite belong to the orthorhombic system. The curious absence of a crystal structure of herapathite has been expressed (13). Past difficulties in its determination presumably arose from lamellar twinning and the complexity of the formula unit. In the absence of a crystal structure, we are not certain how herapathite functions as a dichroic polarizer. This is a vexing and remarkably long-standing (>150 years) question. West and

others (13–15) speculated that a linear arrangement of the iodides might explain the enormous dichroic ratio. Spectra in polarized light were given by Land and West (16).

Crystals of herapathite were grown from quinine, concentrated sulfuric acid, and I_2 in 1:1 ethanol:acetic acid (3). Herapath-like needles ripened on standing in the mother liquor such that the absorbing axis became more elongated (12) (figs. S4 and S5). The crystals were analyzed with an x-ray diffractometer at room temperature. The orthorhombic cell parameters were $a = 15.2471(3)$ (estimated standard deviations) Å, $b = 18.8854(4)$ Å, and $c = 36.1826(9)$ Å. The crystal structure was solved and refined in the space group $\text{P}2_12_1$. Crystallographic data are summarized in table S1. The quinine configuration established the absolute structure. The asymmetric unit (fig. S1) of our crystals has an acetic acid molecule not captured in Jørgensen's formula (9). Smirnov argued that herapathite is not one substance but a family of related solvates and salts with varying component stoichiometries (15).

The crystal structure is shown in Fig. 1. The six water molecules are distributed over



eight sites, and the acetic acid molecule is distributed over two sites associated with disorder in the quinine vinyl group. The ensemble has a diad axis along a and an approximate diad within the asymmetric unit broken by the dissymmetry in the positions of the iodine atoms. The two triiodide ions lie roughly parallel to the b axis, a feature apparently deduced from powder data (17). Our data give intertriiodide bond lengths of

3.74 and 3.81 Å and intratriiodide distances from 2.89 to 3.01 Å.

In all crystals examined, the b axis is the most absorbing direction. Even though herapathite does not have an obvious visible chromophore, triiodide salts are often richly colored (18). This is a consequence of the association of triiodide ions in extended chains (19) with exciton interactions along the chain length that significantly shift the absorption bands to lower energy, as in model starch-iodine complexes (20). Likewise, delocalized, excitations among many I_3^- ions, polarized along b rather than along the I_3^- ions themselves, account for the remarkable light-absorbing properties of herapathite, confirming the speculation of others (12, 14, 15).

The papers of Herapath (1, 3) and Jørgensen (9) cited herein indicate many related dichroic substances that comprise a rich clathrate chemistry.

References and Notes

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Supporting Online Material

www.sciencemag.org/cgi/content/full/324/5933/1407/DC1

Materials and Methods

SOM Text

Figs. S1 to S5

Table S1

References

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