Supplementary Material for

Herapathite

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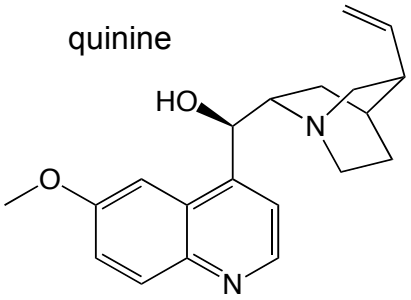
Crystal Structure Determination

Crystals of herapathite were grown from the ethanol/acetic acid liquor containing quinine (see structure below), iodine and sulfuric acid according to the procedure of Herapath cited in the text. The crystal structure of herapathite was established with a Nonius Kappa CCD FR590 single crystal X-ray diffractometer. A clear yellow-gray prism measuring 0.30 x 0.24 x 0.10 mm was mounted on a glass capillary with paratone oil as glue. Data was collected at 298(2)K. The crystal-to-detector distance was set to 42.4 mm. Exposure times were 60 seconds per degree. Data collection was 99.4% complete to 25° in θ. The data was integrated and scaled using hkl-SCALEPACK[1] which applies a multiplicative correction factor (*S*) to the observed intensities (*I*) and has the following form:



$$S = (e^{-2B(\sin^2\theta)/\lambda^2}) / \text{scale}$$

S is calculated from the scale. The *B* factor determined for each frame is then applied to *I* to give the corrected intensity (I_{corr}).

Solution by direct methods (SIR97[2]) produced a partial heavy atom phasing model. The structure was completed by difference Fourier synthesis with SHELXL97[3]. The chemical formula is $4(C_{20}H_{26}N_2O_2)\ .\ C_2H_4O_2\ .\ 3(SO_4^{2-})\ .\ 2(I_3^-)\ .\ 6(H_2O)$. Scattering factors are from Waasmair and Kirfel.[4]

Water hydrogen atoms were attached using a rigid distance model. All other hydrogen atoms were refined using a riding model. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares.

The absolute structure assignment was established via anomalous scattering. The Flack enantiopole parameter[5] was 0.01(3).

Table S1 summarizes the crystal and data collection parameters. Figures S1 shows the ORTEP of the asymmetric unit. Figures S2 and S3 show the packing along the principal axes.

Table S1: Crystallographic data

Herapathite	**$C_{82}H_{120}I_6N_8O_{28}S_3$**
Formula Weight	2523.44
Temperature (*K*)	298(2)
Wavelength (Å)	0.71073
Habit/color	prism / yellow-gray
Crystal System, space group	Orthorhombic, $P22_12_1$ (No. 18)
Unit Cell Dimensions: ***a*, Å** ***b*, Å** ***c*, Å**	 15.2471(3) 18.8854(4) 36.1826(9)
Volume (Å^3)	10418.7(4)
Density g/cm^3	1.609
Reflections Collected/Unique	43120 / 18612
R_{int}/R_s	0.1154 / 0.1855
θ_m/completeness	25° / 99.4%
Final *R* Indices [$I>2\sigma(I)$]: R_1 , wR_2	0.0744, 0.1709
R indices (all data): R_1 , wR_2	0.1837, 0.2054
GOOF	1.003/1.000

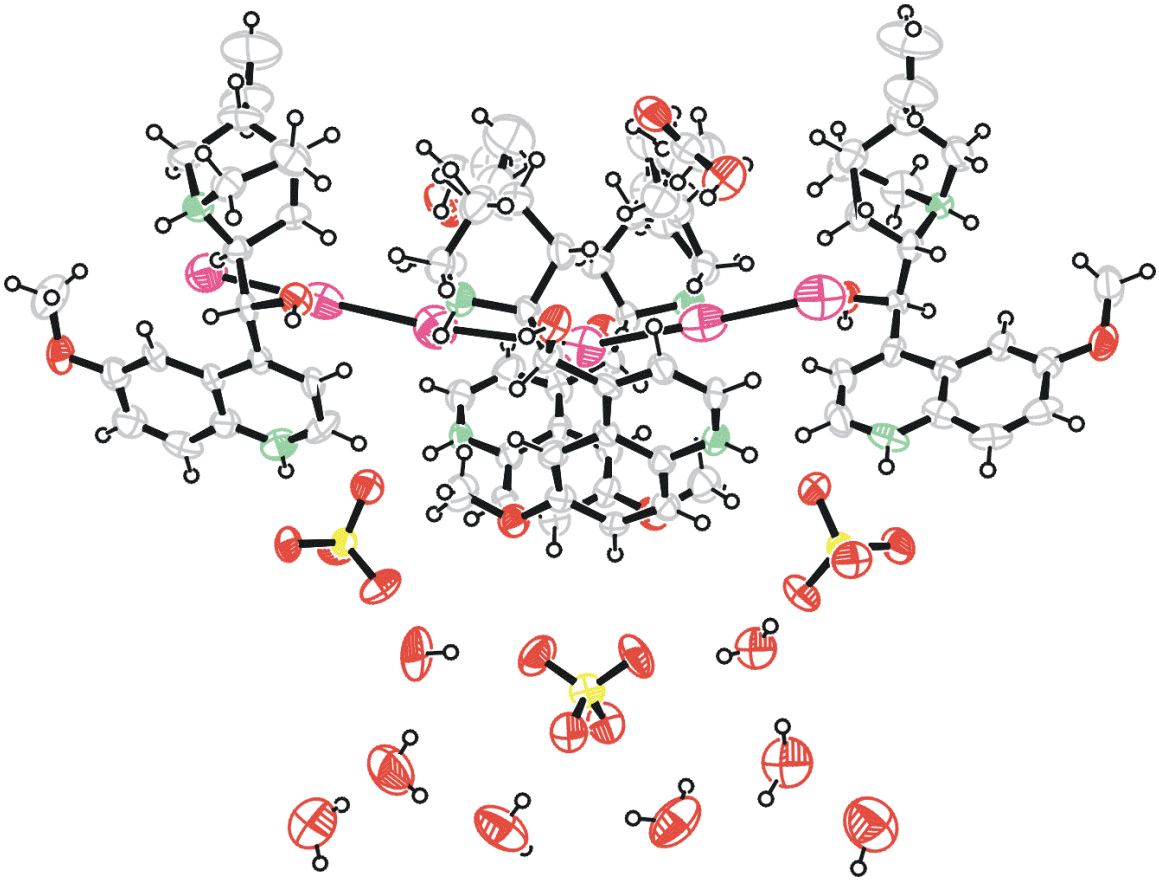


Figure S1. ORTEP of the asymmetric unit along *c*-axis; *a*-axis vertical.

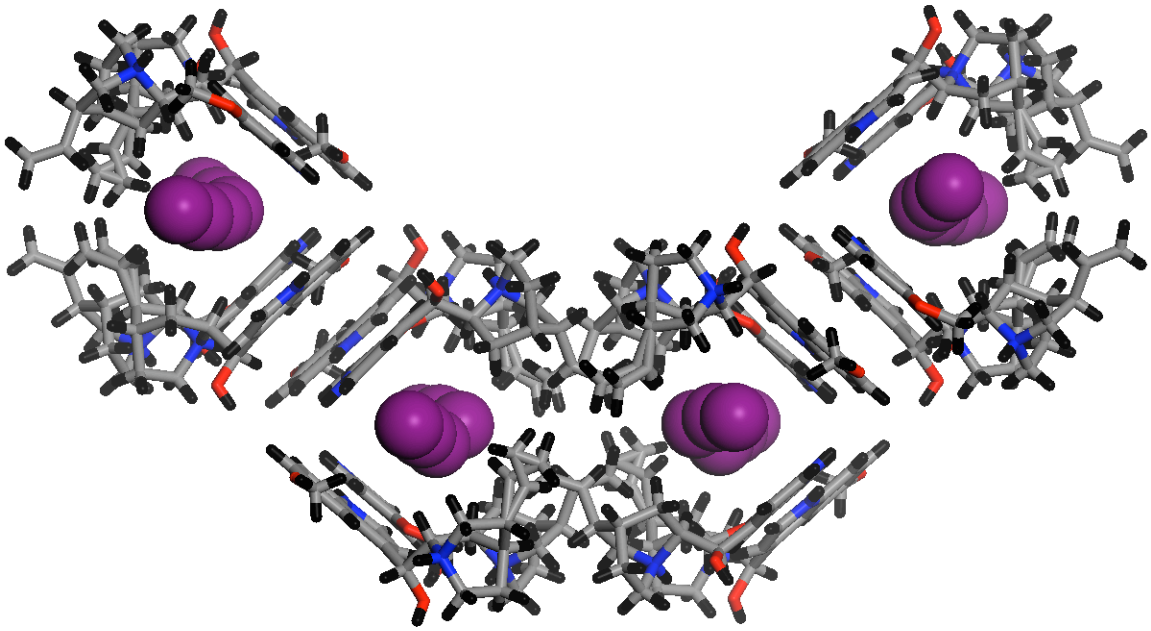


Figure S2. Packing along *b*-axis; *a*-axis vertical. Solvents and counter ions omitted for clarity.

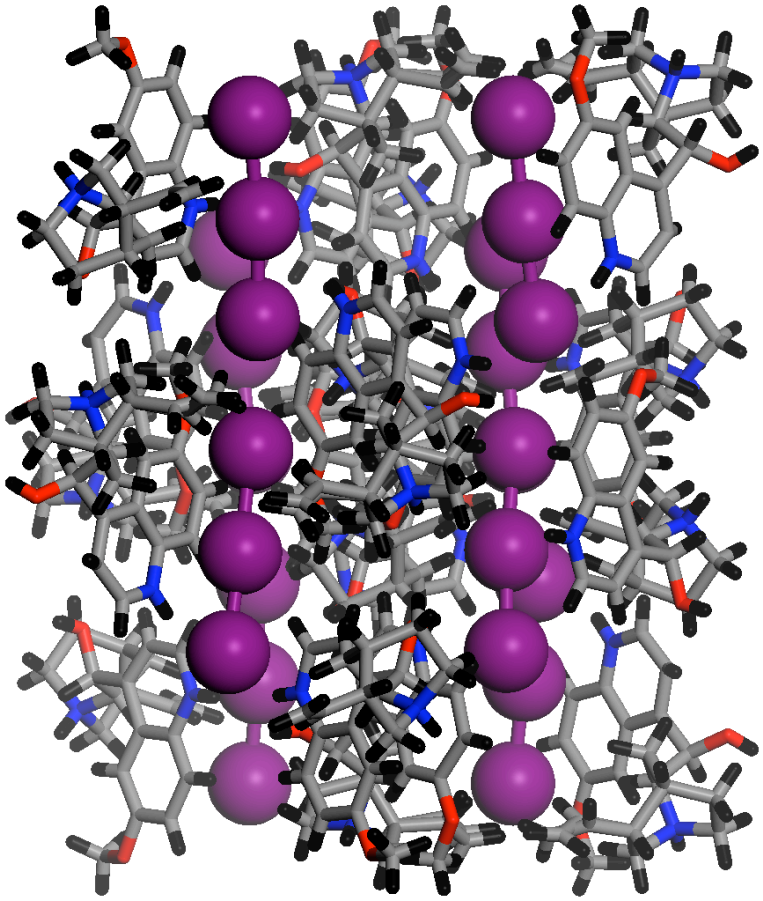


Figure S3. Packing along *a*-axis; *b*-axis vertical. Solvents and counterions omitted for clarity.

Relationship of habit and dichroism.

According to Herapath (*1*), the crystals were dark when the input polarization was perpendicular to the needle axis. See especially Figure S4A from (*1*). These crystals resembled the first precipitate.

According to West (*10*), sometimes the absorbing direction of the tablet shaped crystals was the long axis and sometimes the short. See Figure S4.B. (*10*).

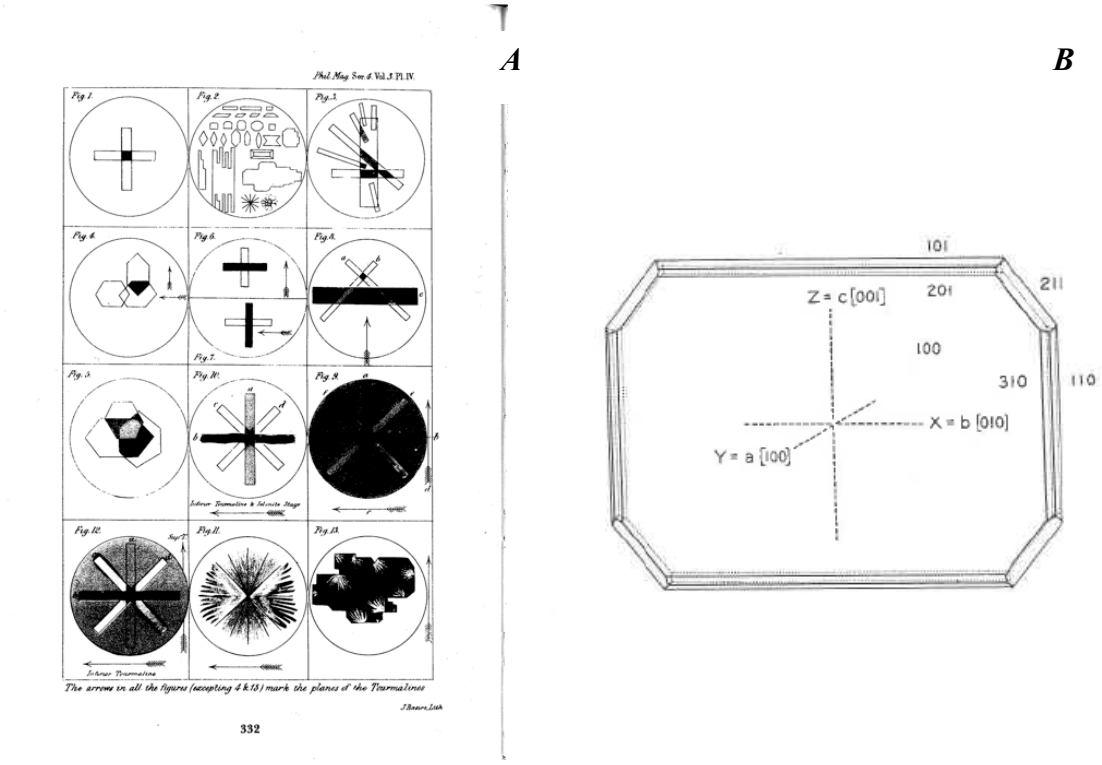


Figure S4. A) Herapath's habits. (*1*) B) West's habit. (*10*)

Our crystal was indexed as well. Most of the samples were yellow-gray, thin, and very fragile, however, after a few days in the mother liquor several more prismatic crystals precipitated. The lattice parameters for both thick and thin crystals were identical and the largest flat face was (001) in each case. Figure S5 shows the morphology although the thickness along [001] is exaggerated for clarity, even for the prisms. West (*10*) reported that for crystals of the general shape reported above, the long direction alternated between *b* and *c*. His *c* axis is that of intermediate length and corresponds to our *b* axis. Our ripened crystals similarly showed *a* or *b* as the longer direction. West's axes and ours can be transformed by cyclic permutation. West's $b \rightarrow$ our a; $c \rightarrow b$; $a \rightarrow c$.

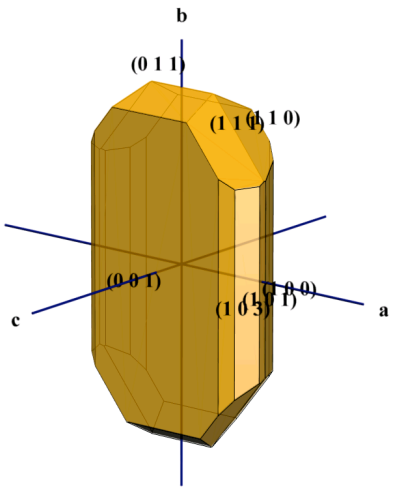


Figure S5. Morphology of our herapathite.[6] The color depends on the sample thickness along [001]. Thinner plates are grayer.

Prediction of morphology with the Bravais-Friedel; Donnay-Harker model[7] shows the faces in following order from largest to smallest: (001), (011), (100), (101), (110), (111) in fairly good agreement with the experimental indexing.

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1. (a) Z. Otwinowsky, W. Minor, Methods Enzymol. 276, 307 (1997).
   (b) S. Mackay, C. Edwards, A. Henderson, C. Gilmore, N. Stewart, K. Shankland, A. Donald, University of Glasgow, Scotland, 1997.
2. A. Altomare, C. Burla, M. Camalli L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, J. Appl. Cryst. 32, 115 (1999).
3. G, M. Sheldrick, SHELXTL97, University of Gottingen, Germany (1997).
4. D. Waasmaier, A. Kirfel, Acta Crystallogr. A. 51, 416 (1995).
5. H. D. Flack, Acta Cryst. A39, 876 (1983).
6. W. Kaminsky, J. Appl. Crystallogr. 38, 566 (2005).
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