Crystal structure of abelsonite, the only known crystalline geoporphyrin

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ABSTRACT

The crystal structure of the uniquenickel porphyrin mineral abelsonite, NiC31H32N4, has been solved using direct methods with 2195 independent reflections to a final $R_1 = 0.0406$. Abelsonite crystallizes in the triclinic space group $P\overline{1}$, with $Z = 1$ and unit-cell parameters $a = 8.4416(5)$ Å, $b = 10.8919(7)$ Å, $c = 7.2749(4)$ Å, $\alpha = 90.465(2)^\circ$, $\beta = 113.158(2)^\circ$, and $\gamma = 78.080(2)^\circ$ at the measurement condition of 100 K, in very good agreement with previous unit-cell parameters reported from powder diffraction. The structure consists of nearly planar, covalently bonded porphyrin molecules stacked approximately parallel to (111), and held together by weak intermolecular Van der Waals forces. The molecules within a layer are slightly tilted such that molecular planes do not overlap, and an up-turned ethyl group on one molecule sits adjacent to a down-turned ethyl group on a neighboring molecule of the same layer. Layers are stacked along a vector normal to (111) such that an aromatic ring at one corner of the molecule lies directly above the opposite aromatic ring of the molecule below. Although a single molecule does not quite possess $T$ symmetry, matching ethyl groups at roughly opposite ends of the molecule enable orientational disorder, in which molecules can randomly adopt one of two different orientations while still stacking in the same manner. The aggregate of these two random orientations produces an overall symmetry of $P\overline{1}$.

Keywords: Abelsonite, crystal structure, porphyrin, geoporphyrin, organic, orientational disorder

INTRODUCTION

Abelsonite is a nickel(II) porphyrin mineral first observed by Trudell (1970) from fractured bedding planes of the Mohogany Zone oil shale in the Green River formation, Uintah County, Utah. Using optical and electron microscopy, electron microprobe, powder X-ray diffraction, UV-vis spectroscopy, IR spectroscopy, and mass spectrometry, Milton et al. (1978) characterized the new material and determined the chemical formula (NiC31H32N4), unit cell, cleavage, and even proposed a structure for the porphyrin molecule that forms the basis of the abelsonite crystal structure. Later, Storm et al. (1984) used proton nuclear magnetic resonance (NMR) spectroscopy to determine the structure of the abelsonite molecule, which was different than that proposed by Milton et al. (1978) only in minor details. Although other geoporphyrin compounds are known, no others occur naturally in the crystalline state, making abelsonite the only recognized geoporphyrin mineral.

Due to the molecule’s similarity to the chlorophyll $a$ molecule, and the abundance of the latter in most plant-derived organic matter, Mason et al. (1989) argue that abelsonite was likely the result of diagenesis of chlorophyll $a$ in anoxic lakes of the Uinta Basin during the Eocene, which was later transported via aqueous solution into its current host shales in the Green River Formation (see Fig. 1 for a comparison of the molecules). Although a synthesis procedure for abelsonite using standard techniques has been reported (Zhang and Lash 2003), the exact mechanisms of chlorophyll diagenesis, and especially the mechanism for the highly selective replacement of Mg by Ni responsible for the natural occurrence of abelsonite, remain unknown. Despite previous work characterizing abelsonite and its geologic environment, as well as crystal structure determinations for other closely related metalloporphyrins (Pettersen 1969, 1971), there has been no determination of the abelsonite crystal structure. Here, we report a complete structure determination for abelsonite, the only known crystalline geoporphyrin, using single-crystal X-ray diffraction coupled with structure solution and refinement using direct methods.

EXPERIMENTAL METHODS

A single crystal of natural abelsonite, with approximate dimensions $40 \times 90 \times 90$ μm, was measured with a Bruker D8 VENTURE diffractometer equipped with a multilayer mirror monochromator and a MoKα microfocus sealed tube with $\lambda = 0.71073$ Å. A total of 24 224 reflections were collected at a voltage of 50 kV and a current of 1.0 mA in the $0$ interval from $2.69^\circ$ to $25.30^\circ$. Temperature was controlled at 100 ± 2 K to minimize thermal broadening of reflections. A total of 2195 unique reflections were harvested from the 24 224 measured reflections (average redundancy 11.036, completeness 99.9%, $R_{int} = 5.27\%$, $R_{exp} = 2.33\%$). Reflections were indexed with $|h| \leq 10$, $|k| \leq 13$, $|l| \leq 8$. Table 1 provides relevant data collection, structure solution, and structure refinement parameters.

The structure was solved using SHELXS-97 (Sheldrick 2008), and then refined using SHELXL-2014/7 (Sheldrick 2015) in space group $P\overline{1}$ using $Z = 1$ and an empirical formula of NiC31H32N4 yielding $R_1 = 0.0406$ for data $F_{o} > 2\sigma(F_{o})$. A refinement in $P\overline{1}$ [$R_1 = 0.055$ for data $F_{o} > 2\sigma(F_{o})$] also yielded a reasonable goodness of fit and featured the same pattern of molecular stacking as the $P\overline{1}$ refinement. However, goodness of fit parameters were consistently better for the $P\overline{1}$ refinement despite having fewer model parameters. Consequently, this refinement was chosen as the correct structure. Because individual H atoms are too electron poor to locate