REVISION 1

Crystal structure of abelsonite, the only known crystalline geoporphyrin

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Abstract

The crystal structure of the unique nickel porphyrin mineral abelsonite, $NiC_{31}H_{32}N_4$, 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-1, with Z=1 and unit cell parameters a = 8.4416 (5) Å, b = 10.8919 (7) Å, c = 7.2749 (4) Å, α = 90.465 (2)^o, β = 113.158 (2)^o, and γ = 78.080 (2)^o 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 ($1\bar{1}1$), 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 ($1\bar{1}1$) 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 $\bar{1}$ 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 $P\bar{1}$.

Introduction

Abelsonite is a nickel (II) porphyrin mineral first observed by Trudell (1970) from fractured bedding planes of the Mahogany 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 ($NiC_{31}H_{32}N_4$), 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 Figure 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 μm x 90 μm x 90 μm, was measured with a Bruker D8 VENTURE diffractometer equipped with a multilayer mirror monochromator and a Mo K_{α} 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 θ interval from 2.69° to 25.30°. Temperature was controlled at 100 $\pm$ 2 K in order 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%, $R_{int} = 5.27\%$, $R_{sig} = 2.33\%$). 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-1 using Z = 1 and an empirical formula of $NiC_{31}H_{32}N_4$, yielding $R_1 = 0.0406$ (for data $F_o > 2\sigma(F_o)$). A refinement in P1 ($R_1 = 0.055$ 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 $P\bar{1}$ refinement. However, goodness of fit parameters were consistently better for the $P\bar{1}$ 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 using laboratory X-ray methods, the H atoms were allowed to ride their parent C atoms during refinement.

Description of the Structure

The refined unit cell parameters at T =100 K were a = 8.4416 (5) Å, b = 10.8919 (7) Å, c = 7.2749 (4) Å, α = 90.465 (2)°, β = 113.158 (2)°, and γ = 78.080 (2)°, with Z = 1 in space group $P\bar{1}$. Refinement parameters are tabulated in Table 1. The unit cell settings for abelsonite were chosen to be consistent with the unit cell reported by Milton et al. (1978), which is the "reduced" cell with the shortest non-colinear translations, and non-acute interedge angles α and β. The values reported here all agree within 2.1% relative error with the values reported by Milton et al. (1978).

The structure of the porphyrin molecule found in our structure solution is identical to that deduced by Storm et al. (1984) using proton NMR spectroscopy (Fig. 1A). The molecule consists of a 20-carbon porphyrin ring with five methyl groups at the 2, 3, 7, 12, and 18 positions, two terminal ethyl groups at the 8 and 17 positions, a bridging ethyl group connecting the 13 and 15 positions on the outer side of the ring, and four nitrogen atoms bridging the 1 and 4, 6 and 9, 11 and 14, and 16 and 19 positions on the inner side of the ring (using standard porphyrin nomenclature). The IUPAC name for the compound is therefore (2,3,7,12,18-pentamethyl-8,17-diethylcyclopenta[mno]porphyrinato)nickel(II). The numbering scheme adopted in our tables and figures is different in order to highlight atoms related by the inversion center, and the nature of the orientational disorder (see Figures 1A and 2).

The Ni^{2+} cation sits in the center of the ring, and is covalently bonded to the four pyrrole nitrogen atoms, as normally seen in metalloporphyrin compounds (Cheng et al. 2003). The inversion center (about which the two distinct molecular orientations are centered) is located at the Ni position of (½, ½, ½). Interestingly, the Ni1-N2 distance (1.92 Å) is noticeably shorter than the Ni1-N1 distance (1.97 Å). This is likely due to strain induced by the exocyclic ring formed by atoms C15 and C16, as observed for other metalloporphyrins with this same structural feature (Pettersen 1969, 1971). The positions of the majority of atoms in the molecule are very nearly coplanar, except that the ethyl group composed of atoms C13 and C14' (Fig. 1A) is up-turned such that C14' lies on one side of the plane, while the ethyl group composed of atoms C11 and C12 is down-turned such that C12 lies on the other side of the plane. Atomic coordinates and isotropic displacement parameters are provided in Table 2, and anisotropic displacement parameters are in Table 3.

Porphyrin molecules within the abelsonite crystal structure are all oriented approximately parallel to the $(1\bar{1}1)$ crystallographic plane (Fig. 3). This orientation explains the single $(1\bar{1}1)$ cleavage plane noted by Milton et al. (1978). However, adjacent molecules within the same "layer" have molecular planes which are tilted relative to the layer, so that molecular planes are offset by ~1.38 Å normal to the plane of the molecule. Thus, across many unit cells the overall layer is exactly parallel to $(1\bar{1}1)$, while the plane of an individual molecule is at a slight angle to $(1\bar{1}1)$. This staggered configuration is a consequence of adjacent molecules being positioned corner-to-corner such that the up-turned ethyl group (C13 and C14') of one molecule sits adjacent to the down-turned ethyl group (C11 and C12) of the neighboring molecule. Thus, each layer of molecules forms an array in which molecules line up corner-to-corner, similar to known synthetic metalloporphyrins (e.g. Pettersen, 1971; Stevens, 1981; Hazen et al. 1987). These corners of neighboring molecules are bound to each other by weak Van der Waals interactions between ethyl groups along approximately [110], and between methyl groups (C14) along the other diagonal of the molecule, approximately $[\bar{1}11]$.

Abelsonite exhibits orientational disorder in its structure, similar to other metalloporphyrins (e.g., Hunter et al., 2014). The matched ethyl groups on nearly opposite corners of the abelsonite porphyrin likely assist in enabling a crystalline, translational structure in which molecules are free to take one of two different orientations without significantly affecting the free energy of the crystal. This structural feature, together with the high degree of specificity of this porphyrin for Ni(II) (Milton et al. 1978), contribute to abelsonite's ability to form a pure, crystalline metalloporphyrin compound in a natural setting, making it unique in the mineral kingdom. It is a fitting historical coincidence that the first and third authors of this contribution currently work (and the fourth author formerly worked) at the Geophysical Laboratory, where the mineral's namesake, organic geochemist Philip H. Abelson, was director from 1953-1971.

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Table 1: Data collection and structure refinement parameters for abelsonite.

Chemical Formula	$NiC_{31}H_{32}N_4$	
Formula weight	519.306 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal Size	40 x 90 x 90 μm	
Crystal System	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 8.4416(5) Å	α = 90.465(2)^o
	b = 10.8919(7)Å	β = 113.158(2)^o
	c = 7.2749(4) Å	γ = 78.080(2)^o
Unit cell volume	599.74(6) Å^3	
Z	1	
Density (calculated)	1.438 g/cm^3	
Absorption coefficient	0.838 mm^{-1}	
F(000)	274	
Diffractometer	Bruker D8 VENTURE	
Radiation source	Microfocus sealed tube, Mo K_α	
Theta range	2.69 – 25.30^o	
Index range	$-10 \leq h \leq 10$; $-13 \leq k \leq 13$; $-8 \leq l \leq 8$	
Reflections collected	24224	
Independent reflections	2195	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-scan	
Transmission range	0.9261-0.9664	
Structure solution technique	Direct Methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2015)	
Function minimized	$\Sigma\, w(F_o^2-F_c^2)^2$	
Data/Restraints/Parameters	2195 / 346 / 304	
Goodness of fit on F^2	1.034	
Final R indices	1911 data with $F_o>2\sigma(F_o)$	R_1 = 0.0406, wR_2 = 0.0942
	All data	R_1 = 0.0514, wR_2 = 0.1019
Weighting scheme	$w=1/[\sigma^2F_o^2+(0.0415P)^2+0.5633P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.00(3)	
Largest diffraction peak and hole	0.548 and -0.481 Å^{-3}	
R.M.S. deviation from mean	0.052 Å^{-3}	

Table 2: Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for abelsonite. (U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor; Numbers in parentheses are the 1σ errors for the final digits of the value; Values for H atoms have no errors because they were allowed to ride their parent C atoms during refinement.)

Atom	x/a	y/b	z/c	U(eq)
Ni1	0.5	0.5	0.5	0.0445(2)
N1	0.6443(3)	0.6220(3)	0.5051(3)	0.0506(6)
N2	0.4250(3)	0.5918(3)	0.6893(3)	0.0474(6)
C1	0.7537(4)	0.6235(3)	0.4030(5)	0.0581(8)
C2	0.8650(11)	0.7047(9)	0.4766(16)	0.0284(19)
C3	0.8030(11)	0.7754(8)	0.6030(16)	0.0392(19)
C4	0.6804(12)	0.7115(9)	0.6304(17)	0.036(2)
C5	0.5907(19)	0.7476(12)	0.753(2)	0.042(3)
C11	0. 0013(14)	0.7364(11)	0.4079(18)	0.036(2)
C12	0.9157(13)	0.8402(9)	0.2374(13)	0.054(2)
C13	0.8520(15)	0.8926(9)	0.6995(17)	0.053(3)
C15	0.1597(19)	0.6141(14)	0.9728(18)	0.049(3)
C16	0.1160(9)	0.4961(6)	0.8515(11)	0.0616(17)
C6	0.4658(4)	0.6994(3)	0.7770(4)	0.0505(7)
C7	0.3796(4)	0.7354(3)	0.9134(4)	0.0497(7)
C8	0.2847(3)	0.6483(3)	0.9057(4)	0.0460(7)
C9	0.3137(3)	0.5612(3)	0.7692(4)	0.0483(7)
C10	0.2280(4)	0.4642(3)	0.7277(5)	0.0566(8)
C14	0.3975(5)	0.8462(4)	0. 0357(5)	0.0655(9)
C2’	0.816(2)	0.7507(12)	0.437(2)	0.066(4)
C3’	0.751(3)	0.804(2)	0.552(4)	0.054(8)
C4’	0.6330(13)	0.7453(11)	0.5908(16)	0.046(3)
C5’	0.5548(18)	0.7837(13)	0.724(2)	0.051(3)
C11’	0.9529(17)	0.7716(12)	0.3585(19)	0.065(3)
C13’	0.800(3)	0.923(2)	0.642(3)	0.053(5)
C14’	0.730(2)	0.0224(14)	0.543(2)	0.067(4)
C15’	0.177(2)	0.6322(15)	0.0340(19)	0.054(3)
C2”	0.801(5)	0.732(5)	0.407(5)	0.050(8)
C11”	0.855(3)	0.805(2)	0.270(4)	0.028(5)
C12”	1.055(3)	0.780(2)	0.355(4)	0.047(7)
C3”	0.731(4)	0.8328(18)	0.540(5)	0.049(5)
C13”	0.744(3)	0.9651(18)	0.604(3)	0.055(5)
C14”	0.9138(17)	0.9606(12)	0.8025(18)	0.042(4)
H5	0.6222	0.8161	0.8303	0.05
H11A	0. 0574	0.6602	0.3623	0.043
H11B	0. 0946	0.7641	0.522	0.043
H12A	0.8251	0.812	0.1235	0.08

H12B	0. 0058	0.8594	0.196	0.08
H12C	0.8611	0.9158	0.283	0.08
H13A	0.9661	0.8996	0.7002	0.079
H13B	0.8606	0.888	0.8377	0.079
H13C	0.7612	0.9666	0.6235	0.079
H15A	0.053	0.6828	0.9382	0.059
H15B	0.2126	0.5917	0.1193	0.059
H16A	0.14	0.4229	0.9459	0.074
H16B	0.9891	0.514	0.761	0.074
H10	0.1518	0.4573	0.7927	0.068
H14A	0.4755	0.892	0.0088	0.098
H14B	0.2809	0.9021	0.0002	0.098
H14C	0.4477	0.8174	0.1784	0.098
H14D	0.3272	0.849	0.1161	0.098
H14E	0.5219	0.8389	0.1248	0.098
H14F	0.3551	0.9236	0.9465	0.098
H5’	0.56	0.8631	0.7785	0.061
H11D	0.8969	0.787	0.2121	0.097
H11E	0.0496	0.6967	0.396	0.097
H11F	0.9997	0.8445	0.4171	0.097
H13D	0.777	0.9297	0.7659	0.08
H13E	0.9291	0.9125	0.6843	0.08
H14G	0.7523	0.0196	0.4211	0.101
H14H	0.777	0.09	0.6212	0.101
H14I	0.6019	0.0384	0.5071	0.101
H1	0.0747	0.9543	0.3399	0.071
H2	0.9813	0.0831	0.2820	0.071
H3	0.0966	0.0862	0.4111	0.071
H15D	0.0519	0.6417	0.9453	0.08
H15E	0.1891	0.6964	0.1307	0.08
H15F	0.2222	0.5483	0.1059	0.08
H11G	0.8088	0.7777	0.1322	0.034
H11H	0.8049	0.8966	0.2636	0.034
H12D	0.0986	0.8158	0.4848	0.07
H12E	0.0924	0.8187	0.2621	0.07
H12F	0.1035	0.6889	0.3729	0.07
H13F	0.6374	0. 0052	0.6265	0.066
H13G	0.7494	0. 0165	0.4958	0.066
H14J	0.9017	0.9186	0.9133	0.063
H14K	0.9272	0.0466	0.8334	0.063
H14L	0.0182	0.9138	0.784	0.063

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Table 3: Anisotropic displacement parameters for non-hydrogen atoms in abelsonite. (Numbers in parentheses are the 1σ errors for the final digits of the value.)

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Ni1	0.0268(3)	0.0813(4)	0.0345(3)	-0.0229(2)	-0.0165(2)	0.0126(2)
N1	0.0427(13)	0.0856(18)	0.0423(13)	-0.0330(12)	0.0276(11)	-0.0145(12)
N2	0.0254(10)	0.0832(17)	0.0385(12)	-0.0181(11)	0.0149(9)	-0.0120(11)
C1	0.0625(19)	0.085(2)	0.0592(18)	-0.0461(17)	0.0439(16)	-0.0227(16)
C2	0.013(3)	0.035(4)	0.031(4)	-0.001(3)	0.006(3)	0.002(3)
C3	0.025(3)	0.054(4)	0.040(5)	-0.012(3)	0.013(3)	-0.008(3)
C4	0.020(4)	0.050 (4)	0.034(4)	-0.005(3)	0.009(4)	-0.001(3)
C5	0.028(4)	0.053(5)	0.045(5)	-0.006(3)	0.015(4)	-0.007(4)
C11	0.026(3)	0.041(4)	0.042(4)	-0.011(3)	0.015(3)	-0.002(3)
C12	0.051(5)	0.071(6)	0.044(4)	-0.026(4)	0.018(4)	0.003(4)
C13	0.042(5)	0.063(5)	0.062(6)	-0.024(4)	0.024(4)	-0.021(4)
C15	0.041(4)	0.054(5)	0.067(7)	-0.014(3)	0.037(5)	-0.010(4)
C16	0.064(4)	0.071(4)	0.085(4)	-0.034(3)	0.058(4)	-0.025(3)
C6	0.0352(14)	0.091(2)	0.0367(14)	-0.0315(14)	0.0175(12)	-0.0183(14)
C7	0.0401(14)	0.080(2)	0.0411(15)	-0.0285(14)	0.0221(12)	-0.0160(13)
C8	0.0340(13)	0.0663(18)	0.0486(15)	-0.0184(12)	0.0245(12)	-0.0143(13)
C9	0.0296(13)	0.0740(19)	0.0466(15)	-0.0152(13)	0.0192(12)	-0.0133(13)
C10	0.0482(17)	0.089(2)	0.0562(18)	-0.0305(16)	0.0380(15)	-0.0147(16)
C14	0.073(2)	0.096(3)	0.0571(19)	-0.052(2)	0.0417(17)	-0.0300(18)
C2′	0.093(9)	0.076(7)	0.075(8)	-0.058(6)	0.063(8)	-0.029(6)
C3′	0.062(15)	0.072(9)	0.047(15)	-0.035(10)	0.031(14)	-0.012(10)
C4′	0.036(6)	0.085(6)	0.029(4)	-0.031(5)	0.015(5)	-0.007(4)
C5′	0.054(8)	0.085(8)	0.033(5)	-0.041(7)	0.025(6)	-0.020(5)
C11′	0.067(7)	0.086(7)	0.071(7)	-0.047(6)	0.043(6)	-0.017(5)
C13′	0.070(14)	0.073(8)	0.048(9)	-0.037(7)	0.047(9)	-0.017(6)
C14′	0.104(10)	0.060(7)	0.056(7)	-0.040(7)	0.040(7)	-0.020(6)
C15′	0.059(5)	0.066(7)	0.059(7)	-0.027(4)	0.042(5)	-0.014(4)
C2″	0.062(18)	0.071(8)	0.048(15)	-0.036(10)	0.045(15)	-0.017(8)
C11″	0.022(10)	0.037(10)	0.040(10)	-0.014(8)	0.023(8)	-0.003(7)
C12″	0.032(10)	0.061(15)	0.054(13)	-0.018(8)	0.022(9)	0.010(11)
C3″	0.064(12)	0.063(7)	0.043(9)	-0.029(7)	0.040(9)	-0.008(6)
C13″	0.055(7)	0.059(7)	0.052(6)	-0.015(4)	0.022(4)	-0.006(4)
C14″	0.052(6)	0.043(6)	0.043(5)	-0.020(5)	-0.020(5)	-0.011(4)

Table 4: Bond distances in abelsonite. (Numbers in parentheses indicate 1σ errors in the final digits of the values. Values without errors were fixed during refinement.)

Bond	Distance (Å)	Bond	Distance (Å)
Ni1-N2	1.923(2)	C9-C10	1.367(4)
Ni1-N2	1.923(2)	C10-C1	1.371(4)
Ni1-N1	1.970(2)	C10-H10	0.95
Ni1-N1	1.970(2)	C14-H14A	0.98
N1-C4	1.328(12)	C14-H14B	0.98
N1-C1	1.397(3)	C14-H14C	0.98
N1-C4'	1.477(12)	C14-H14D	0.98
N2-C6	1.372(4)	C14-H14E	0.98
N2-C9	1.376(3)	C14-H14F	0.98
C1-C2"	1.32(4)	C2'-C3'	1.25(3)
C1-C10	1.371(4)	C2'-C11'	1.534(7)
C1-C2	1.376(11)	C3'-C4'	1.403(15)
C1-C2'	1.565(11)	C3'-C13'	1.510(15)
C2-C3	1.383(11)	C4'-C5'	1.390(10)
C2-C11	1.520(8)	C5'-H5'	0.95
C3-C4	1.434(9)	C11'-H11D	0.98
C3-C13	1.506(9)	C11'-H11E	0.98
C4-C5	1.387(10)	C11'-H11F	0.98
C5-C6	1.340(14)	C13'-C14'	1.21(3)
C5-H5	0.95	C13'-H13D	0.99
C11-C12	1.523(12)	C13'-H13E	0.99
C11-H11A	0.99	C14'-H14G	0.98
C11-H11B	0.99	C14'-H14H	0.98
C12-H12A	0.98	C14'-H14I	0.98
C12-H12B	0.98	C15'-H15D	0.98
C12-H12C	0.98	C15'-H15E	0.98
C13-H13A	0.98	C15'-H15F	0.98
C13-H13B	0.98	C2"-C11"	1.532(10)
C13-H13C	0.98	C2"-C3"	1.63(6)
C15-C8	1.436(12)	C11"-C12"	1.519(19)
C15-C16	1.578(13)	C11"-H11G	0.99
C15-H15A	0.99	C11"-H11H	0.99
C15-H15B	0.99	C12"-H12D	0.98
C16-C10	1.534(6)	C12"-H12E	0.98
C16-H16A	0.99	C12"-H12F	0.98
C16-H16B	0.99	C3"-C13"	1.522(15)
C6-C5'	1.440(14)	C13"-C14"	1.58(2)
C6-C7	1.453(4)	C13"-H13F	0.99
C7-C8	1.350(4)	C13"-H13G	0.99
C7-C14	1.491(4)	C14"-H14J	0.98
C8-C9	1.424(4)	C14"-H14K	0.98
C8-C15'	1.571(11)	C14"-H14L	0.98

Table 5: Bond angles in abelsonite. (Numbers in parentheses indicate 1σ errors in the final digits of the values. Values without errors were fixed during refinement.)

Bond pair	Angle (°)	Bond pair	Angle (°)
N2-Ni1-N2	180	C7-C14-H14B	109.5
N2-Ni1-N1	89.68(10)	H14A-C14-H14B	109.5
N2-Ni1-N1	90.32(10)	C7-C14-H14C	109.5
N2-Ni1-N1	90.32(10)	H14A-C14-H14C	109.5
N2-Ni1-N1	89.68(10)	H14B-C14-H14C	109.5
N1-Ni1-N1	180	C7-C14-H14D	109.5
C4-N1-C1	103.4(5)	H14A-C14-H14D	141.1
C1-N1-C4'	104.6(4)	H14B-C14-H14D	56.3
C4-N1-Ni1	127.1(5)	H14C-C14-H14D	56.3
C1-N1-Ni1	128.9(2)	C7-C14-H14E	109.5
C4'-N1-Ni1	125.7(4)	H14A-C14-H14E	56.3
C6-N2-C9	103.5(2)	H14B-C14-H14E	141.1
C6-N2-Ni1	130.27(18)	H14C-C14-H14E	56.3
C9-N2-Ni1	126.2(2)	H14D-C14-H14E	109.5
C2"-C1-C10	122.7(17)	C7-C14-H14F	109.5
C10-C1-C2	123.3(5)	H14A-C14-H14F	56.3
C2"-C1-N1	112.6(19)	H14B-C14-H14F	56.3
C10-C1-N1	122.8(3)	H14C-C14-H14F	141.1
C2-C1-N1	112.7(5)	H14D-C14-H14F	109.5
C10-C1-C2'	128.8(5)	H14E-C14-H14F	109.5
N1-C1-C2'	107.5(5)	C3'-C2'-C11'	135.7(13)
C1-C2-C3	105.1(7)	C3'-C2'-C1	105.0(10)
C1-C2-C11	129.9(9)	C11'-C2'-C1	118.5(9)
C3-C2-C11	123.7(10)	C2'-C3'-C4'	115.5(16)
C2-C3-C4	105.1(8)	C2'-C3'-C13'	121.1(17)
C2-C3-C13	129.4(9)	C4'-C3'-C13'	123.(2)
C4-C3-C13	125.5(9)	C5'-C4'-C3'	125.1(15)
N1-C4-C5	122.5(11)	C5'-C4'-N1	126.6(10)
N1-C4-C3	112.1(8)	C3'-C4'-N1	106.8(12)
C5-C4-C3	124.9(11)	C4'-C5'-C6	117.9(11)
C6-C5-C4	129.1(13)	C4'-C5'-H5'	121
C6-C5-H5	115.5	C6-C5'-H5'	121
C4-C5-H5	115.5	C2'-C11'-H11D	109.5
C2-C11-C12	110.8(8)	C2'-C11'-H11E	109.5
C2-C11-H11A	109.5	H11D-C11'-H11E	109.5
C12-C11-H11A	109.5	C2'-C11'-H11F	109.5
C2-C11-H11B	109.5	H11D-C11'-H11F	109.5
C12-C11-H11B	109.5	H11E-C11'-H11F	109.5
H11A-C11-H11B	108.1	C14'-C13'-C3'	119.2(17)
C11-C12-H12A	109.5	C14'-C13'-H13D	107.5
C11-C12-H12B	109.5	C3'-C13'-H13D	107.5
H12A-C12-H12B	109.5	C14'-C13'-H13E	107.5
C11-C12-H12C	109.5	C3'-C13'-H13E	107.5

H12A-C12-H12C	109.5	H13D-C13'-H13E	107
H12B-C12-H12C	109.5	C13'-C14'-H14G	109.5
C3-C13-H13A	109.5	C13'-C14'-H14H	109.5
C3-C13-H13B	109.5	H14G-C14'-H14H	109.5
H13A-C13-H13B	109.5	C13'-C14'-H14I	109.5
C3-C13-H13C	109.5	H14G-C14'-H14I	109.5
H13A-C13-H13C	109.5	H14H-C14'-H14I	109.5
H13B-C13-H13C	109.5	C8-C15'-H15D	109.5
C8-C15-C16	101.5(6)	C8-C15'-H15E	109.5
C8-C15-H15A	111.5	H15D-C15'-H15E	109.5
C16-C15-H15A	111.5	C8-C15'-H15F	109.5
C8-C15-H15B	111.5	H15D-C15'-H15F	109.5
C16-C15-H15B	111.5	H15E-C15'-H15F	109.5
H15A-C15-H15B	109.3	C1-C2"-C11"	135.(3)
C10-C16-C15	110.6(6)	C1-C2"-C3"	114.(2)
C10-C16-H16A	109.5	C11"-C2"-C3"	108.(3)
C15-C16-H16A	109.5	C12"-C11"-C2"	108.(2)
C10-C16-H16B	109.5	C12"-C11"-H11G	110
C15-C16-H16B	109.5	C2"-C11"-H11G	110
H16A-C16-H16B	108.1	C12"-C11"-H11H	110
C5-C6-N2	119.9(6)	C2"-C11"-H11H	110
N2-C6-C5'	127.3(6)	H11G-C11"-H11H	108.4
C5-C6-C7	127.9(7)	C11"-C12"-H12D	109.5
N2-C6-C7	111.5(2)	C11"-C12"-H12E	109.5
C5'-C6-C7	120.3(6)	H12D-C12"-H12E	109.5
C8-C7-C6	105.9(3)	C11"-C12"-H12F	109.5
C8-C7-C14	128.6(3)	H12D-C12"-H12F	109.5
C6-C7-C14	125.5(3)	H12E-C12"-H12F	109.5
C7-C8-C9	106.7(2)	C13"-C3"-C2"	139.(2)
C7-C8-C15	144.3(5)	C3"-C13"-C14"	110.5(19)
C9-C8-C15	108.8(5)	C3"-C13"-H13F	109.6
C7-C8-C15'	128.9(5)	C14"-C13"-H13F	109.6
C9-C8-C15'	124.1(5)	C3"-C13"-H13G	109.6
C10-C9-N2	128.5(3)	C14"-C13"-H13G	109.6
C10-C9-C8	119.2(3)	H13F-C13"-H13G	108.1
N2-C9-C8	112.3(3)	C13"-C14"-H14J	109.5
C9-C10-C1	123.3(3)	C13"-C14"-H14K	109.5
C9-C10-C16	99.7(3)	H14J-C14"-H14K	109.5
C1-C10-C16	136.8(3)	C13"-C14"-H14L	109.5
C9-C10-H10	118.3	H14J-C14"-H14L	109.5
C1-C10-H10	118.3	H14K-C14"-H14L	109.5
C7-C14-H14A	109.5		

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Figure Captions

Figure 1: A) Structure of the abelsonite porphyrin molecule. Black = C; Blue = N; Green = Ni, Pink = H. Hydrogen atoms are not labeled on the diagram to preserve clarity, but are listed in Table 2 and named using the same number as the carbon atom to which they are bonded. Only one orientation of the molecule is shown in this figure – complete unit cell contents showing $P\bar{1}$ symmetry is show in Figure 2. B) Structure of the chlorophyll *a* molecule for comparison. Black = C; Blue = N; Orange = Mg; Red = O; Pink = H. The orientation of the alkane chain with respect to the porphyrin ring has been rotated to preserve clarity.

Figure 2: Complete unit cell contents of the abelsonite crystal structure with all non-hydrogen atoms labeled. Black = C; Blue = N; Green = Ni, Pink = H. Closely spaced atoms which are colored partly white and have alternative labeling with 'prime' symbols (') indicate atoms with partial occupancy, which are present in one orientation of the molecule but not the other (i.e., in a single physical molecule, either atom C15 or C15' is present, but not both). The aggregate of atomic positions over a large number of unit cells produces $P\bar{1}$ symmetry, even though a single molecule lacks $\bar{1}$ symmetry. The molecule is tilted out of the plane of the page in order to more clearly show closely overlapping atomic positions.

Figure 3: Projection of the abelsonite crystal structure on approximately $(10\bar{1})$. Black = C; Blue = N; Green = Ni, Pink = H. Arrows show the unit cell vectors; Black lines show location of the unit cell; Blue plane shows $(1\bar{1}1)$ stacking plane; Black double arrow shows the vertical offset of porphyrin molecules due to tilting within the layer. Not all of each molecule is shown due to the

limited *hkl* range of the model. Although molecules in the real abelsonite structure can adopt one of two different inverted orientations, molecules shown here are in the same orientation to preserve clarity.

Figure 4: Projection of the abelsonite crystal structure approximately on the stacking plane $(1\bar{1}1)$, showing two molecular layers. Black = C; Blue = N; Green = Ni, Pink = H. Arrows show the unit cell vectors; Black lines show location of the unit cell; Blue plane shows $(1\bar{1}1)$ stacking plane (in the plane of the page). Note aromatic rings of one molecule superimposed over aromatic rings of another molecule. Not all molecules are complete due to the limited *hkl* range of the model. Although molecules in the real abelsonite structure can adopt one of two different inverted orientations, molecules shown here are in the same orientation to preserve clarity.

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Figure 1A

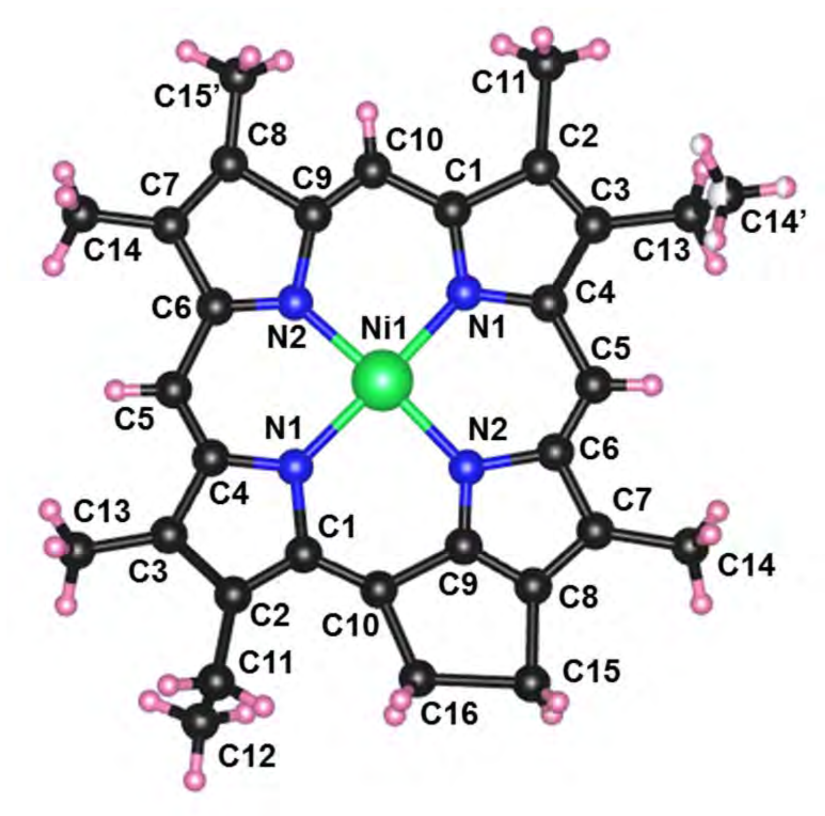


Figure 1B

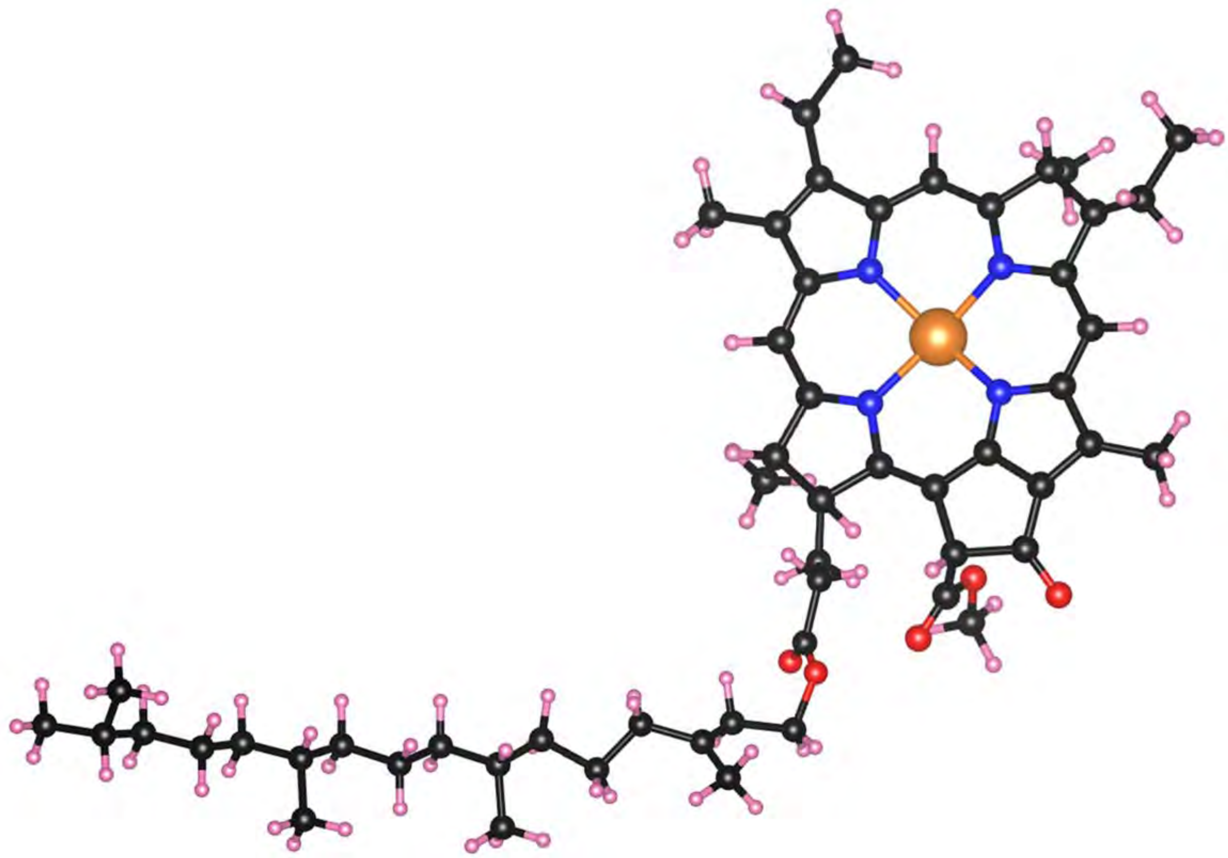
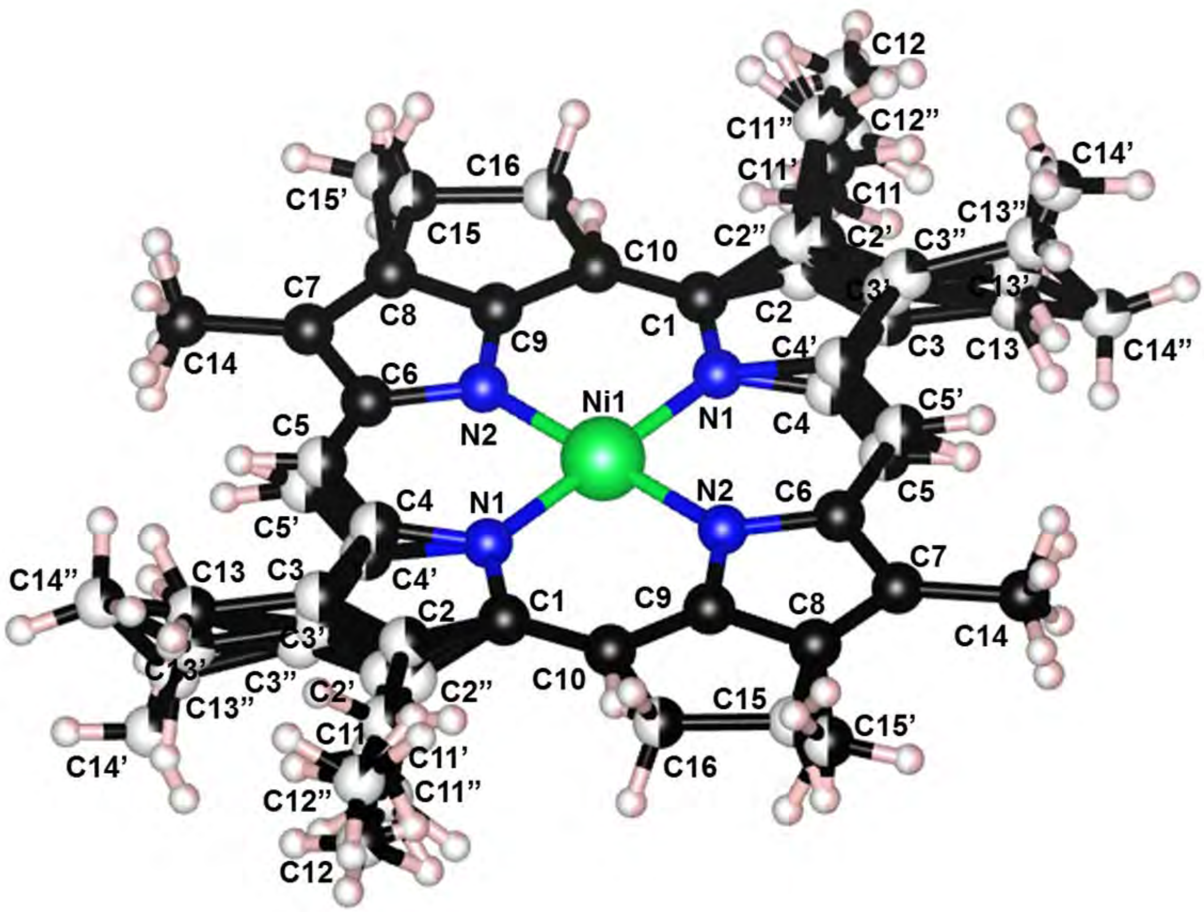


Figure 2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C11"
C12"
C14'
C11'
C11
C16
C15'
C15
C13"
C2"
C2'
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C10
C3'
C13'
C7
C8
C9
C1
C2
C3
C13
C14"
C14
C6
C4'
Ni1
N1
C5'
C5
N2
C4
N2
C6
C5
N1
C4
C5'
C7
C14"
C13
C3
C4'
C1
C9
C8
C2
C14
C3'
C13'
C3"
C2'
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C11"
C16
C12

Figure 3

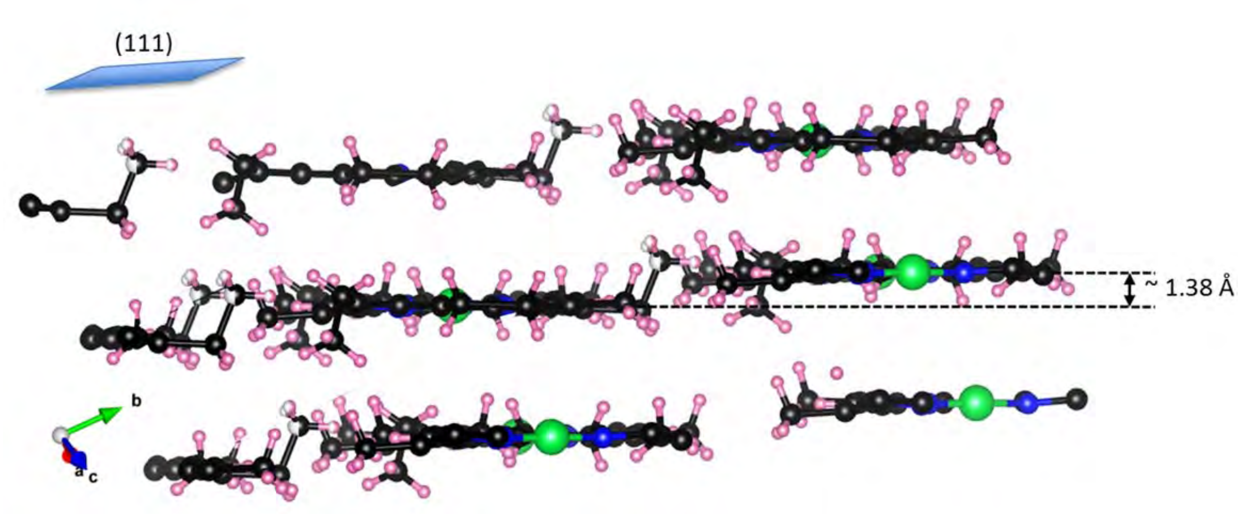

Figure 4