Synchrotron X-ray Investigation of α -Chlorohemin, $C_{34}H_{32}ClFeN_4O_4$, an Fe-porphyrin

J.A. Kaduk¹, W. Wong-Ng^{2*}, L.P. Cook³, B. Chakraborty³, S. H. Lapidus⁴, L. Ribaud⁴, G. Brewer³, ¹Chemistry Department, Illinois Institute of Technology, Chicago, IL 60616; ²Materials Measurement Science Division, National Institute of Standards and Technology, Gaithersburg, MD, 20899; ³Chemistry Department, The Catholic University of America, Washington, DC 20064; and ⁴Advanced Photon Source, Argonne National laboratory, Argonne, IL 60439.

*Corresponding author: Winnie.wong-ng@nist.gov

Abstract

X-ray data of a powder sample of α -chlorohemin (a member of the porphyrin family), $C_{34}H_{32}ClFeN_4O_4$, was collected using synchrotron radiation at the Advanced Photon Source (APS, Argonne National Laboratory). Rietveld Refinement and Density Functional Theory (DFT) calculations were performed for obtaining the structure including positions of hydrogen atoms. The structure was found to be $P-1$, $Z = 2$; at 100K the lattice parameters are $a = 11.22468(6)$ Å, $b = 13.93930(8)$ Å, $c = 10.79818(9)$ Å, $\alpha = 99.6672(6)^\circ$, $\beta = 108.4124(8)^\circ$, $\gamma = 106.7175(6)^\circ$, and $V = 1471.713(19)$ Å³, and at 295K, $a = 11.43217(7)$ Å, $b = 14.06412(10)$ Å, $c = 10.85390(9)$ Å, $\alpha = 98.6655(7)^\circ$, $\beta = 108.6294(8)^\circ$, $\gamma = 107.5025(7)^\circ$, and $V = 1517.21(2)$ Å³, $D_x = 1.427$ g/cm³. Experimental reference X-ray patterns have also been determined, which will be included in the Powder Diffraction File (PDF).

Keywords: α -chlorohemin, $C_{34}H_{32}ClFeN_4O_4$; crystal structure; synchrotron powder diffraction; MOFs; Rietveld Refinements; DFT calculations

Introduction

Research on metal organic frameworks (MOFs) and other porous materials has been an intense world-wide activity in recent years for various environmental, energy and sustainability applications [1-13]. MOF compounds are built from metal ions (or *in situ* generated metal clusters) that are interconnected by multi-dentate organic ligands via coordinate bonds to generate two-or three-dimensional periodic networks featuring controllable channels or cages [14]. Their pore size, pore walls, surface area and other structural features can be tailored by custom design of organic linkers.

Porphyrins and metalloporphyrins can be used as a basis for synthesizing MOFs. They are among the most extensively studied materials because of their biological importance and wide range of applications (sensors, gas storage, and heterogeneous catalysis). In the area of gas capture/storage, a great number of MOFs were developed based on custom-designed porphyrin ligands. Therefore in recent years the structures of porphyrins have received renewed interest.

The metal-metalloporphyrin frameworks (MMPFs) are essentially a type of MOFs. According to Gao et al. [15, 16], the driving force behind the growth of MMPFs is twofold. The first lies in the salient features of porphyrin and metalloporphyrin molecules such as their highly thermal and chemical stabilities, robust nature, and facile synthesis [17-20]. Therefore they have great potential as building blocks in the construction of coordination polymers. At the same time, metalloporphyrins are one of the cornerstones on which the existence of life is based [18]. The first porphyrin-based MOF dated back to as early as 1991 as reported by Abrahams et al. [21]. Ma and his coworker have conducted systematic studies of a great number of MOFs based on the metalloporphyrin framework [14-16, 22-25]. Porphyrin-based MOFs have exhibited potential for applications in gas storage/separation [3], light harvesting [26], catalysts [27], and other applications [28, 29].

The chemical designation of α -chlorohemin (1, 3, 5, 8-tetramethyl-2,4-divinylporphine-6,7-dipropionic acid ferrichloride) has several synonyms: ‘chloro(protoporphyrinato) iron(III)’, ‘chloroproteoporphyrin IX iron(III)’, and ‘ferriproteoporphyrin IX chloride’. Figures 1a and 1b give the schematic drawing of α -chlorohemin and protonated-porphyrin, respectively. The first

structure determination of α -chlorohemin was conducted by Koenig in 1965 [30]. Since the structure was not completed at that time, we re-determined the structure at 100K (liq. N₂ as coolant) and at room temperature (RT) using the powder synchrotron X-ray technique. As X-ray diffraction is a non-destructive technique for phase identification, X-ray diffraction patterns are especially important for phase characterization. Currently only an unindexed reference pattern, which was submitted in 1958, is included in the Powder Diffraction File (PDF, 2015) as a primary pattern (PDF 8-761) [31]. The intensity values of this reported pattern were estimated only visually. As accurate digital data is important for computational and analysis purposes, a re-measurement of α -chlorohemin using state-of-the-art diffraction techniques is important for the scientific community.

The first goal of our project is to re-investigate the crystal structure of a powder sample of α -chlorohemin, C₃₄H₃₂ClFeN₄O₄, using synchrotron radiation at the Advanced Photon Source (APS, Argonne National Laboratory). The second goal of this investigation is to determine the experimental pattern for α -chlorohemin at both RT and at 100K using the Rietveld refinement techniques [32, 33], and to make them widely available through submission to the PDF. Density Functional Theory (DFT) calculation was performed on this compound for confirming the stability of the structure and to determine the atomic positions of the hydrogen atoms.

Experimental¹

I. Sample.

A black powder sample of α -chlorohemin, C₃₄H₃₂ClFeN₄O₄ (1,3,5,8-tetramethyl-2,4-divinylporphine-6,7-dipropionic acid ferrichloride) was obtained commercially from SIGMA-ALDRICH (lot # SLBJ2248V, CAS 16009-13-5, from bovine); reported MW is 651.96/mol. The sample was loaded into a capillary tubing provided by the Advanced Photon Source (APS), Argonne National Laboratory.

---

¹ The purpose of identifying the equipment and software in this article is to specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology.

II. High resolution synchrotron Diffraction

High resolution synchrotron X-ray powder diffraction data were collected using beamline 11-BM at the APS using a wavelength of 0.413802 Å at 100K (with N₂ as coolant) and at RT. Discrete detectors covered a final angular range from 0° to 50°, with data points collected every 0.001° in 2θ at a scan speed of 0.01°/s. The instrumental optics of 11-BM incorporate two platinum-stripped mirrors and a double-crystal Si (111) monochromator, where the second crystal has an adjustable sagittal bend [34]. The diffractometer is controlled via EPICS [35]. A vertical Huber 480 goniometer positions 12 perfect Si (111) analyzers and 12 Oxford-Danfysik LaCl₃ scintillators, with a spacing of 2° in 2θ [36]. Capillary samples are mounted by a robotic arm and spun at ≈ 90 Hz. Data are normalized to incident flux and collected while continually scanning the diffractometer 2θ arm. A mixture of National Institute of Standard and Technology standard reference materials, Si (SRM^{TM} 640c) and Al₂O₃ (SRM^{TM} 676) [37], is used to calibrate the instrument, where the Si lattice constant determines the wavelength for each detector. Corrections are applied for detector sensitivity, 2θ offset, and small detector wavelength differences, before merging the data into a single set of intensities evenly spaced in 2θ.

III. DFT Calculations

To obtain a good starting model for Rietveld refinements including hydrogen atoms, a density functional geometry optimization (fixed experimental unit cell) was carried out to obtain the structure at 100K including the hydrogen atoms using CRYSTAL09 [38]. The basis sets for the H, C, N, and O atoms were those of Gatti *et al.* [39], the basis set for Cl was that of Apra *et al.* [40], and the basis set for Fe was from Valerio *et al.* [41]. The calculation used 8 *k*-points and the B3LYP functional, and took ~95 days on a 2.4 GHz PC. CSD Refcode CHEMIN [30] was then used by adding missing hydrogen atoms using Materials Studio 7.0 [42].

IV. Rietveld Refinements

Using the result of the DFT calculation, Rietveld refinement was carried out using GSAS [32, 43]. Only the 1.7-25.0° portion of the pattern was included in the refinement ($d_{min} = 0.955$ Å). All non-H bond distances and angles were subjected to restraints, based on a Mercury/Mogul Geometry Check [44, 45] of the molecule. The Mogul average and standard deviation for each quantity were used as the restraint parameters. Planar restraints were applied to the four C₄N

rings of the core. The restraints contributed 8.08% to the final χ^2 . Isotropic displacement coefficients were refined, grouped by chemical similarity. The hydrogen atoms were included in calculated positions, which were recalculated during the refinement. The U_{iso} of each hydrogen atom was constrained to be 1.3 fold that of the heavy atom to which it is attached. Initial positions of the active hydrogens were deduced from an analysis of potential hydrogen bonding patterns. The peak profiles were described using profile function #4 [46, 47], which includes the Stephens' anisotropic strain broadening model [48]. The background was modeled using a 3-term shifted Chebyshev polynomial, with a 5-term diffuse scattering function to model the Kapton capillary and any amorphous component. A 2nd-order spherical harmonic preferred orientation model was included; the texture index was only 1.011. The final refinement (started from the result of the DFT calculation) of 174 variables using 23427 observations (23302 data points and 125 restraints) yielded the residuals $R_{wp} = 0.0762$, $R_p = 0.0625$, and $\chi^2 = 2.961$. For the structure at 300K, the starting model was that of the DFT 100K, the same refinement strategy was applied.

Reference patterns were obtained with a Rietveld pattern decomposition technique. Using this technique, the reported peak positions were derived from the extracted integrated intensities, and positions calculated from the lattice parameters. When peaks are not resolved at the resolution function, the intensities are summed, and an intensity-weighted d-spacing is reported.

Results and Discussion

Figure 2 gives the experimental X-ray pattern for α -chlorohemin taken at RT. The observed (crosses), calculated (solid line), and difference XRD patterns (bottom) are illustrated. The difference pattern is plotted at the same scale as the other patterns. Above $10.5^\circ 2\theta$ (synchrotron wavelength of wavelength of $0.413802 \text{ \AA}$), the vertical scale of all patterns has been magnified five times. The row of tick marks indicates the calculated peak positions. There is no evidence of sample decay after the synchrotron X-ray irradiation as no peak position shifting was observed.

The Rietveld refinement results are within acceptable range (For the 100K structure: $R=0.0625$, $wR=0.0762$, Goodness of fit=1.721; for the RT structure: $R=0.0762$, $wR=0.0933$, Goodness of fit=1.50). Results of the Rietveld refinements for α -chlorohemin are reported in Table 1 to Table

3. Tables 1a and 1b give the atomic coordinates for α -chlorohemin for the structure determined at 100K and at RT. In Table 1a (100K), the hydrogen positions are also given. The hydrogen positions for the structure determined at RT are taken from those determined at 100K. Tables 2a (100K) and 2b (RT) give the selected bond distances.

The structure was found to be triclinic $P-1$, $Z = 2$; at 100K the lattice parameters are $a = 11.22468(6)$ Å, $b = 13.93930(8)$ Å, $c = 10.79818(9)$ Å, $\alpha = 99.6672(6)^\circ$, $\beta = 108.4124(8)^\circ$, $\gamma = 106.7175(6)^\circ$, and $V = 1471.71(2)$ Å³, $D_x = 1.471$ g/cm³. For the RT sample, $a = 11.43217(7)$ Å, $b = 14.06412(10)$ Å, $c = 10.85390(9)$ Å, $\alpha = 98.6655(7)^\circ$, $\beta = 108.6294(8)^\circ$, $\gamma = 107.5025(7)^\circ$, and $V = 1517.21(2)$ Å³, $D_x = 1.427$ g/cm³. As expected, it was found that the unit cell parameters are slightly larger at RT than at 100K ($V = 1517.21(2)$ Å³ at RT vs. $V = 1471.71(2)$ Å³ at 100K).

The overall structure of α -chlorohemin agrees with that reported by Koenig [30]. Figure 4 gives the labeling scheme of the structure including hydrogen atoms. The salient feature of the structure is the pyramidal arrangement of the $[\text{FeN}_4\text{Cl}]$ moiety where the Fe atom is five-coordinate including the Cl atom as one of the apex. The four nitrogen atoms form a near square planar and each of the N is a member of the planar pyrrole rings. The pyramidal arrangements of the $[\text{FeN}_4\text{Cl}]$ moiety (determined using data collected at 100K and at RT) are depicted in Fig. 5a and Fig. 5b. The four nitrogen atoms nearly form a square planar array within 0.01 Å along the normal through the center of the square [30]. The chlorine atom lies on the other side of the plane that is opposite to the Fe atom. The pyramidal (Fe-N) distances are 2.078 (4) Å, 2.066(4) Å, 2.060(4) Å, 2.103(3) Å (100K), and 2.100(4) Å, 2.089(4) Å, 2.047(4) Å, 2.091(4) Å (RT), respectively. The distance between Fe and Cl is at a longer 2.304 (3) Å (100K) than that of 2.283 (4) Å at RT. The distances between each of the four Cl...N and N...N pairs are also indicated in Fig. 5a and Fig. 5b. All the pyrrole rings are planar. The porphyrin ring, is, however puckered, with each of the pyrrole ring tilted with respect to each other. For example, Table 3 gives the inter-planar angles between the planes of pyrrole ring for Hemin at 100K. The distance of the Fe out of the mean plane is about 0.5 Å [30].

Intermolecular hydrogen bonding is observed in the structure. The carboxyl groups of propionate moieties attaching to the pyrrole rings in one molecule are hydrogen-bonded to carboxyl groups in the other molecule. Figure 6a shows a packing view of the structure along the c -axis without

hydrogens, while Fig. 6b shows the hydrogen bonding between the carboxyl groups of two α -chlorohemin molecules in close proximity. The hydrogen bond distances are found to be 2.918 Å for O61-H70...O60; 2.732 Å for O59-H69...O62 at 100K; and 2.616 Å and 2.657 Å at RT, respectively.

Reference x-ray diffraction pattern

In these patterns, the symbols 'M' and '+' refer to peaks containing contributions from two and more than two reflections, respectively. The particular peak that has the strongest intensity in the entire pattern is assigned an intensity of 999 and other lines are scaled relative to this value. In general, the d-spacing values are calculated values from refined lattice parameters. The intensity values reported are integrated intensities (rather than peak heights) based on the corresponding profile parameters as reported in Table 4. For resolved overlapped peaks, intensity-weighted calculated d-spacing, along with the observed integrated intensity and the *hkl* indices of both peaks (for 'M'), or the *hkl* indices of the strongest peak (for '+') are used. For peaks that are not resolved at the instrumental resolution, the intensity-weighted average d-spacing and the summed integrated intensity value are used. In the case of a cluster, unconstrained profile fits often reveal the presence of multiple peaks, even when they are closer than the instrumental resolution. In this situation, both d-spacing and intensity values are reported independently. All patterns have been submitted for inclusion in the PDF.

Summary

The structure and reference powder X-ray diffraction patterns for a porous metalloporphyrin, α -chlorohemin ($C_{34}H_{32}ClFeN_4O_4$), have been redetermined using synchrotron X-ray diffraction data collected at the Advanced Photo Source (APS) of the Argonne National Laboratory, at both RT and at 100K. The X-ray patterns have been submitted to the PDF of ICDD for publication. We are interested in pursuing further research in the Cr-, Co- and Cu- analogs of Fe-porphyrin IV in the near future.

References

1. O.M. Yaghi, Q. Li, MRS Bulletin, **34** (2009) 682-690.
2. B. Wang, A.P. Cote, H. Furukawa, M.J. O’Keeffe, and O.M. Yaghi, Nature, **453** (2008) 207.
3. R.E. Morris, P.S. Wheatley, Angew. Chem. Int. Ed. **47** (2008) 4966-4981.
4. H. Furukawa, K.E. Cordova, M. O’Keeffe, O.M. Yaghi, Science, **341** (2013), 1230444-1 to 1230444-12.
5. C. Dey, T. Kundu, B.P. Biswal, A. Mallick, R. Banerjee, Acta Cryst. **B70** (2014) 3-10.
6. H.C. Zhou, S. Kitagawa, Chem. Soc. Rev., **43** (2014) 5415-5418.
7. L. Espinal, L., W. Wong-Ng, J.A. Kaduk, A.J. Allen, C.R. Snyder, D.W. Siderius, L. Li, E. Cockayne, A.E. Espinal, S.L. Suib, J. Amer. Chem. Soc., **134**(8) (2012) 7944-51.
8. L. Espinal, D.L. Poster, W. Wong-Ng, A.J. Allen, M. Green, Environmental Science and Technol. **47** (2013) 11960-11975.
9. K.L. Kauffman, J.T. Culp, J. Allen, L. Espinal-Thielen, W. Wong-Ng, T.D. Brown, A. Goodman, M.O. Bernardo, R. J. Pancoast, D. Chirdon, and C. Matranga, Angew Chem. Int. Ed. **50** (2011) 10888-10892.
10. W. Wong-Ng, J.A. Kaduk, H. Wu, M.R. Suchomel, Powder Diffr. **27**(4) (2012) 256-262.
11. W. Wong-Ng, J.A. Kaduk, Q. Huang, L. Espinal, L. Li, J.W., Burrell, Microporous and Mesoporous Materials, **172** (2013) 95-104.
12. W. Wong-Ng, J.T. Culp, Y.S. Chen, P. Zavalij, L. Espinal, D.W. Siderius, A.J. Allen, S. Scheins, C. Matranga, CryEngComm., **15** (2013) 4684-4693

13. W. Wong-Ng, J.A. Kaduk, I. Levin, L. Espinal, D.L. Siderus, A.L. Allen, M. Suchkumel, *Powd. Diffr.* **30**(1) (2015) 2-13.
14. W.-Y. Gao, and S. Ma, *Comments on Inorganic Chemistry: A Journal of Critical Discussion of the Current Literature*, **34:5-6** (2014) 125-141.
15. W.-Y. Gao, M. Chrzanowski, and S. Ma, *Chem Soc. Rev.* **43** (2014) 5841-5866.
16. W.-Y. Gao, L. Wojtas, & S. Ma, *ChemComm.* **50**, (2014) 5316-5318.
17. C.M. Drain, A. Varotto, and I. Radivojevic, *Chem Rev.*, **109** (2009) 1630-1658
18. K.M. Kadish, K.M. Smith, **Guilard**, *The Porphyrin Handbook*, Academic press, Sa Diego, (2000-2003).
19. I. Beletskaya, V.S. Tyurin, A.Y. Tsivadze, R. Guilard, and S. Cchristine, *Chem. Rev.* **109** (2009) 1659-1713.
20. Y. Nakamura, N. Araatai, and A. Osuka, *Chem. Soc. Rev.* **36** (2007) 831-845.
21. B.F. Abrahams, B.F. Hoskins, and R. Robson, *J. Am. Chem. Soc.* **113** (1991) 3696-3607.
22. L. Meng, Q. Cheng, C. Kim, W.-Y. Gao, L. Wojtas, Y.-S. Chen, M.J. Zaworotko, X.P. Zhang, S. Ma, *Angew. Chem, Int. Ed.* **51** (2012) 10082-10085.
23. X.-S Wang, M. Chrzanowski, C. Jim, W.-Y.Gao, L. Wojtas, Y.-S.Chen, X.P. Zhang, and S. Ma, *Chem. Commum.* **48** (2012) 7173-7175.
24. X.-S Wang, L. Meng, Q. Cheng, C. Kim, L. Wojtas, M. Chrzanowski, Y.-S.Chen, X.P. Zhang, and S. Ma, *J. Am. Chem. Soc.* **133** (2011) 16322-16325.

25. X.-S Wang, M. Chrzanowski, L. Wojtas, Y.-S., Chen, and S. Ma, Chem. Eur. J. **19** (2013) 3297-3301.
26. C.Y. Lee, O.K. Farha, B.J. Hong, A.A. Sarjeant, S.T.. Nguyen, and J.T. Hupp, J. Am. Chem. Soc. **133** (2011) 15858.
27. A. Fateeva, P.A. Chater, C.P. Ireland, A.A., Tahit, Y.Z. KHimyak, P.V. Wiper, J.R. Darwent, and M.J. Rosseinsky, Angew. Chem. Int. Ed., **51** (2012) 7440.
28. W.-Y.Gao, Z., Zhang, L. Cash, L. Wojtas, Y.-S Chen, and S. Ma, CrystEngComm, **15** (2013) 9320.
29. S. Motoyama, R. Makiura, O. Sakata, H. Kitagawa, J.Am. Chem. Soc. **133** (2011) 5460.
30. F. Koenig, Acta Cryst. **18** (1965) 663-673.
31. Powder Diffraction File (PDF), International Centre for Diffraction Data (ICDD), 12 Campus Blvd., Newtown Square, PA 19073-3273, USA (2015).
32. A.C. Larson, R.B. Von Dreele, *General Structure Analysis System (GSAS)*, Los Alamos National Laboratory Report LAUR 86-748, Los Alamos, USA (2004).
33. H.M. Rietveld, J. Appl. Cryst. **2** (1969) 65-71.
34. J. Wang, B.H. Toby, P.L. Lee, L. Ribaud, S. Antao, C. Kurtz, M. Ramanathan, R.B. Von Dreele, and M.A. Beno, Rev. Sci. Instrum. **79** (2008) 085105.
35. L.R. Dalesio, J.O. Hill, M. Kraimer, S. Lewis, D. Murray, S. Hunt, W. Watson, M., Clausen, and J. Dalesio, Nuclear Instruments & Methods in Physics Research Section A-Accelerators Spectrometers Detectors and Associated Equipment **352** (1994) 179-184.

36. P.L. Lee, D. Shu, M. Ramanathan, C. Preissner, J. Wang, M.A. Beno, R.B. Von Dreele, L. Ribaud, C. Kurtz, S.M. Antao, X. Jiao, and B.H. Toby, *J. Synchrotron Radiation* **15** (2008) 427-432.
37. Standard Reference materials (SRM^{TM}) produced at the National Institute of Standards and Technology (NIST). All data and programs are freely available online at <http://srmd.nist.gov/>
38. R. Dovesi, R. Orlando, B., Civalleri, C. Roetti, V.R. Saunders, C.M. and Zicovich-Wilson, *Zeit. Krist.* **220** (2005) 571-573.
39. C. Gatti, V.R. Saunders, and C. Roetti, *J. Chem. Phys.* **101** (1994) 10686-10696.
40. E. Apra E., M. Causa, M. Prencipe, R. Dovesi, and V.R. Saunders, *J. Phys.: Cond. Matt.* **5**(18) (1993) 2969-2976.
41. G. Valerio, M. Catti, R. Dovesi, and R. Orlando, *Phys. Rev.* **B52** (1995) 2422-2427.
42. Accelrys, *Materials Studio 7.0* (Accelrys Software Inc., San Diego CA) (2013).
43. B.H. Toby, EXPGUI, a graphical user interface for GSAS, *J. Appl. Crystallogr.* **34** (2001) 210-213.
44. R.A. Sykes, P. McCabe, F.H. Allen, G.M. Battle, I.J. Bruno, and P.A. Wood, *J. Appl. Crystallogr.* **44** (2011) 882-886.
45. I.J. Bruno, J.C. Cole, M. Kessler, J. Luo, W.D.S. Motherwell, L.H. Purkis, B.R. Smith, R. Taylor, R.I. Cooper, S.E. Harris, and A.G. Orpen, *J. Chem. Inf. Sci.* **44** (2004) 2133-2144.
46. P. Thompson, D.E. Cox, and J.B. Hastings, *J. Appl. Crystallogr.* **20**(2) (1987) 79-83.

47. L.W. Finger, D.E. Cox, and A.P. Jephcoat, *J. Appl. Crystallogr.* **27**(6) (1994) 892-900.

48. P.W. Stephens, *J. Appl. Crystallogr.* **32** (1999) 281-289.

Figure Legends

Fig. 1. (1a) Schematic drawings of α -chlorohemin, and (1b) protonated-porphyrin, respectively.

Fig. 2. Observed (crosses), calculated (solid line), and difference (bottom) XRD patterns for α -chlorohemin by the Rietveld analysis technique. The difference pattern is plotted at the same scale as the other calculated peak positions up to $11^\circ 2\theta$. At higher angles, the scale has been magnified five times.

Fig. 3. The labeling scheme of α -chlorohemin, $C_{34}H_{32}ClFeN_4O_4$. For clarity, a wire model was used to represent the structure.

Fig. 4. The ball and stick representation of the structure of α -chlorohemin, $C_{34}H_{32}ClFeN_4O_4$, with the hydrogen atoms included.

Fig. 5. The pyramidal view (distorted square pyramid) of the FeN_4Cl group in the partial structure of α -chlorohemin. The atomic distances between Cl and N's of the distorted square pyramid are given (a) 100K, and (b) 298K (RT). In both cases, the distances between $Fe\dots N$ are non-bonded distances.

Fig. 6. Two molecules of α -chlorohemin, $C_{34}H_{32}ClFeN_4O_4$, showing (a) hydrogen bonding between the oxygen of one carboxyl group to the hydrogen atom of another carboxyl group, and (b) enlarged view of the content inside the box.

Table 1a. Atomic coordinate and isotropic displacement factors in C₃₄H₃₂ClFeN₄O₄ (100K)

Atom	x	y	z	U _{iso}
C11	0.1430 (3)	0.6664(3)	0.3847(3)	0.0350(14)
C2	0.38063(13)	0.7484(3)	0.1497(3)	0.0153(8)
C3	0.2665(10)	0.3830(4)	0.4172(4)	0.0153(8)
C4	0.34474(9)	0.4722(3)	0.5266(3)	0.0153(8)
C5	0.39904(9)	0.4730(3)	0.6648(4)	0.0153(8)
C6	0.47600(9)	0.5735(3)	0.7378(4)	0.0153(8)
C7	0.46958(9)	0.6360(3)	0.6437(4)	0.0153(8)
C8	0.5402 (9)	0.7439(3)	0.6727(5)	0.0153(8)
C9	0.54342(11)	0.8032(3)	0.5795(3)	-0.001(4)
C10	0.62823(12)	0.9119(3)	0.6106(4)	0.0153(8)
C11	0.61562(12)	0.9377(3)	0.4954(4)	0.0153(8)
C12	0.52118(12)	0.8442(3)	0.3886(3)	0.0153(8)
C13	0.33288(14)	0.7422(4)	0.0070(4)	0.0153(8)
C14	0.4659(8)	0.8390(4)	0.2558(4)	0.0153(8)
C15	0.3912(11)	0.8264(5)	-0.0472(7)	0.074(2)
C16	0.3387(14)	0.8180(8)	-0.1831(9)	0.074(2)
C17	0.1458(10)	0.6082(6)	-0.2139(5)	0.074(2)
C18	-0.0240(11)	0.2531(5)	-0.0818(6)	0.074(2)
C19	0.0794(6)	0.1808(5)	0.1846(6)	0.0397(12)
C20	-0.0364(6)	0.1500(5)	0.2331(7)	0.0397(12)
C21	-0.0839(6)	0.0364(5)	0.2365(7)	0.0397(12)
C22	0.3755(9)	0.3775(5)	0.7136(8)	0.0397(12)
C23	0.23571(14)	0.6471(3)	-0.0636(4)	0.0153(8)
C24	0.2394(7)	0.3491(5)	0.7208(10)	0.0397(12)
C25	0.1880(7)	0.2372(5)	0.7237(7)	0.0397(12)
C26	0.5578(11)	0.6124(5)	0.8878(5)	0.074(2)
C27	0.7369(8)	0.9719(6)	0.7377(6)	0.074(2)
C28	0.7232(10)	0.9884(8)	0.8462(9)	0.074(2)
C29	0.6972(10)	1.0371(4)	0.4744(9)	0.074(2)
C30	0.22224(13)	0.5924(3)	0.0367(4)	0.0153(8)
C31	0.1380(8)	0.4910(3)	0.0098(5)	0.0153(8)
C32	0.14368(10)	0.4292(3)	0.0988(4)	0.0153(8)
C33	0.07497(10)	0.3188(3)	0.0597(4)	0.0153(8)
C34	0.11019(10)	0.2880(3)	0.1739(4)	0.0153(8)
C35	0.20121(9)	0.3803(3)	0.2844(4)	0.0153(8)
Fe36	0.3133(2)	0.6215(2)	0.3470(2)	0.0516(16)
N55	0.31163(14)	0.6556(3)	0.1666(3)	0.0243(8)
N56	0.22051(10)	0.4656(3)	0.2370(4)	0.0243(8)
N57	0.38846(9)	0.5723(3)	0.5147(4)	0.0243(8)
N58	0.47873(11)	0.7635(3)	0.4425(4)	0.0243(8)
O59	-0.2064(6)	-0.0242(5)	0.1582(6)	0.0487(12)
O60	-0.0121(6)	0.0136(5)	0.3271(6)	0.0487(12)
O61	0.0710(6)	0.1723(5)	0.6358(6)	0.0487(12)
O62	0.2536(7)	0.2088(5)	0.8125(7)	0.0487(12)
H37	0.04929	0.12306	0.09244	0.121(3)

H38	0.23086	0.30505	0.43926	0.0199(10)
H39	0.60147	0.78322	0.78219	0.0199(10)
H40	0.52483	0.90561	0.2279	0.0199(10)
H41	-0.01927	0.17301	-0.08829	0.097(2)
H42	0.00666	0.28791	-0.15656	0.097(2)
H43	-0.12575	0.24973	-0.08923	0.097(2)
H44	0.63984	0.68577	0.90744	0.097(2)
H45	0.58891	0.55152	0.9249	0.097(2)
H46	0.48518	0.62882	0.93632	0.097(2)
H47	0.16202	0.17381	0.27387	0.052(2)
H48	-0.12835	0.16661	0.15605	0.052(2)
H49	-0.01594	0.20644	0.33685	0.052(2)
H50	0.45088	0.38879	0.81367	0.052(2)
H51	0.36984	0.30897	0.63499	0.052(2)
H52	0.15845	0.34983	0.63046	0.052(2)
H53	0.24248	0.39836	0.8175	0.052(2)
H54	0.07118	0.44707	-0.09988	0.0199(10)
H63	0.47539	0.90962	0.03461	0.097(2)
H64	0.43687	0.82867	-0.2254	0.097(2)
H65	0.25637	0.81415	-0.23973	0.097(2)
H66	0.14408	0.51828	-0.24641	0.097(2)
H67	0.19259	0.64839	-0.27709	0.097(2)
H68	0.0458	0.59985	-0.2325	0.097(2)
H69	0.81499	1.03582	0.79039	0.097(2)
H70	0.55799	0.92208	0.83781	0.097(2)
H71	0.73408	1.01682	0.97083	0.097(2)
H72	0.6587	1.03128	0.36603	0.097(2)
H73	0.79892	1.05698	0.52747	0.097(2)
H74	0.65911	1.09731	0.5281	0.097(2)
H75	-0.2204	-0.0869	0.177	0.097(2)
H76	0.0505	0.1137	0.6425	0.097(2)

Table 1b. Atomic coordinate and isotropic displacement factors for non-hydrogen atoms in $C_{34}H_{32}ClFeN_4O_4$ (298K).

Atom	x	y	z	U_{iso}
C11	0.1431(5)	0.6598(4)	0.3777(5)	0.083(3)
C2	0.38034(15)	0.7468(4)	0.1460(4)	0.044(2)
C3	0.2721(11)	0.3832(4)	0.4157(5)	0.044(2)
C4	0.34475(9)	0.4726(4)	0.5246(4)	0.044(2)
C5	0.39864(9)	0.4745(4)	0.6646(5)	0.044(2)
C6	0.47553(9)	0.5747(4)	0.7353(4)	0.044(2)
C7	0.46959(9)	0.6354(4)	0.6391(4)	0.044(2)
C8	0.5254(11)	0.7430(4)	0.6683(7)	0.044(2)
C9	0.54260(12)	0.7993(3)	0.5755(4)	0.032(7)
C10	0.62627(12)	0.9072(4)	0.6081(5)	0.044(2)
C11	0.61283(13)	0.9329(4)	0.4912(5)	0.044(2)
C12	0.52003(12)	0.8407(3)	0.3845(4)	0.044(2)
C13	0.3322(2)	0.7416(4)	0.0039(5)	0.044(2)
C14	0.4607(9)	0.8372(4)	0.2511(5)	0.044(2)
C15	0.3962(11)	0.8213(7)	-0.0519(9)	0.148(3)
C16	0.333(2)	0.8385(12)	-0.1627(15)	0.148(3)
C17	0.159(2)	0.6045(7)	-0.2140(5)	0.148(3)
C18	-0.032(2)	0.2547(6)	-0.0744(8)	0.148(3)
C19	0.0758(7)	0.1804(5)	0.1845(7)	0.090(2)
C20	-0.0242(8)	0.1545(6)	0.2494(9)	0.090(2)
C21	-0.0765(9)	0.0409(5)	0.2462(8)	0.090(2)
C22	0.3840(13)	0.3792(6)	0.7146(10)	0.090(2)
C23	0.2358(2)	0.6480(4)	-0.0642(4)	0.044(2)
C24	0.2472(10)	0.3491(7)	0.7203(13)	0.090(2)
C25	0.1922(10)	0.2383(6)	0.7263(9)	0.090(2)
C26	0.563(2)	0.6145(6)	0.8828(6)	0.148(3)
C27	0.7332(9)	0.9626(8)	0.7379(7)	0.148(3)
C28	0.7107(15)	0.9790(12)	0.8444(11)	0.148(3)
C29	0.690(2)	1.0324(5)	0.4707(12)	0.148(3)
C30	0.22228(15)	0.5929(4)	0.0354(4)	0.044(2)
C31	0.1453(10)	0.4894(4)	0.0075(6)	0.044(2)
C32	0.14277(11)	0.4297(4)	0.0981(5)	0.044(2)
C33	0.07500(10)	0.3194(4)	0.0611(5)	0.044(2)
C34	0.11035(9)	0.2886(4)	0.1746(5)	0.044(2)
C35	0.20103(9)	0.3805(3)	0.2837(4)	0.044(2)
Fe36	0.3136(3)	0.6214(2)	0.3463(3)	0.060(2)
N55	0.3113(2)	0.6543(4)	0.1633(4)	0.053(2)
N56	0.21929(9)	0.4659(3)	0.2343(5)	0.053(2)
N57	0.38898(9)	0.5713(4)	0.5108(4)	0.053(2)
N58	0.47865(12)	0.7604(3)	0.4384(5)	0.053(2)
O59	-0.1926(9)	-0.0186(8)	0.1545(10)	0.099(2)
O60	-0.0055(10)	0.0116(7)	0.3289(10)	0.099(2)
O61	0.0762(9)	0.1751(8)	0.6393(10)	0.099(2)
O62	0.2505(10)	0.2100(7)	0.8184(9)	0.099(2)

Table 2a. Selected bond distances (Å) (100K)

Atom	Atom	Distance
C11	Fe36	2.304(3)
C2	C13	1.441(3)
C2	C14	1.396(3)
C2	N55	1.377(3)
C3	C4	1.391(3)
C3	C35	1.377(3)
C4	C5	1.419(3)
C4	N57	1.383(3)
C5	C6	1.354(3)
C5	C22	1.497(4)
C6	C7	1.443(3)
C6	C26	1.497(3)
C7	C8	1.409(3)
C7	N57	1.370(3)
C8	C9	1.409(3)
C9	C10	1.454(3)
C9	N58	1.355(3)
C10	C11	1.329(4)
C10	C27	1.428(4)
C11	C12	1.442(3)
C11	C29	1.522(3)
C12	C14	1.351(3)
C12	N58	1.384(3)
C13	C15	1.476(5)
C13	C23	1.354(4)
C15	C16	1.368(7)
C17	C23	1.517(3)
C18	C33	1.509(3)
C19	C20	1.527(5)
C19	C34	1.468(4)
C20	C21	1.529(3)
C21	O59	1.295(3)
C21	O60	1.210(3)
C22	C24	1.495(5)
C23	C30	1.447(3)
C24	C25	1.509(3)
C25	O61	1.298(3)
C25	O62	1.211(3)
C27	C28	1.222(7)
C30	C31	1.377(3)
C30	N55	1.392(3)
C31	C32	1.393(3)
C32	C33	1.427(3)
C32	N56	1.381(3)
C33	C34	1.352(3)
C34	C35	1.442(3)
C35	N56	1.359(3)
Fe36	N55	2.078(4)

Fe36	N56	2.066(4)
Fe36	N57	2.060(4)
Fe36	N58	2.103(3)

Table 2b. Selected bond distances (Å) (298K (RT))

Atom	Atom	Distance
C11	Fe36	2.283(4)
C2	C13	1.445(3)
C2	C14	1.398(3)
C2	N55	1.378(3)
C3	C4	1.402(3)
C3	C35	1.392(3)
C4	C5	1.438(3)
C4	N57	1.376(3)
C5	C6	1.358(3)
C5	C22	1.505(4)
C6	C7	1.443(3)
C6	C26	1.499(3)
C7	C8	1.394(3)
C7	N57	1.379(3)
C8	C9	1.398(3)
C9	C10	1.446(3)
C9	N58	1.367(3)
C10	C11	1.346(4)
C10	C27	1.443(4)
C11	C12	1.443(3)
C11	C29	1.502(3)
C12	C14	1.375(3)
C12	N58	1.377(3)
C13	C15	1.466(4)
C13	C23	1.345(4)
C15	C16	1.289(7)
C17	C23	1.501(3)
C18	C33	1.505(3)
C19	C20	1.509(4)
C20	C21	1.519(3)
C21	C20	1.519(3)
C21	O59	1.300(3)
C21	O60	1.216(3)
C22	C24	1.516(4)
C23	C30	1.443(3)
C24	C25	1.515(3)
C25	O61	1.295(3)
C25	O62	1.207(3)
C27	C28	1.265(7)
C30	C31	1.382(3)
C30	N55	1.384(3)
C31	C32	1.387(3)
C32	C33	1.435(3)
C32	N56	1.374(3)
C33	C34	1.348(3)
C34	C35	1.447(3)
C35	N56	1.374(3)

Fe36	N55	2.100(4)
Fe36	N56	2.089(4)
Fe36	N57	2.047(4)
Fe36	N58	2.091(4)

Table 3. Interplanar angles between the planes of the pyrrole rings (structure at 100K). Plane 1 contains N56, plane 2 contains N55, plane 3 contains N58, and plane 4 contains N57.

Plane-Plane	Interplanar angle (°)
1-2	17.1
1-3	23.3
1-4	6.0
2-3	11.5
2-4	16.5
3-4	19.6

Table 4. X-ray powder pattern for α -chlorohemin, $C_{34}H_{32}ClFeN_4O_4$ ($P-I$, $Z = 2$; $a = 11.22468(6)$ Å, $b = 13.93930(8)$ Å, $c = 10.79818(9)$ Å, $\alpha = 99.6672(6)^\circ$, $\beta = 108.4124(8)^\circ$, $\gamma = 106.7175(6)^\circ$, and $V = 1471.713(19)$ Å³). Data was collected at 100K. The symbols 'M' and '+' refer to peaks containing contributions from two and more than two reflections, respectively. The particular peak that has the strongest intensity in the entire pattern is assigned an intensity of 999 and other lines are scaled relative to this value. The d-spacing values are calculated values from refined lattice parameters, and 'I' represents integrated intensity values.

d_{cal}	I_{obs}	h	k	l	d_{cal}	I_{obs}	h	k	l	d_{cal}	I_{obs}	h	k	l
12.797	476	0	1	0	9.9184	182	1	0	0	9.8212	133	0	0	1
9.1509	77	0	1	-1	8.9040	692	1	0	-1	7.5567	235	1	-1	-1
7.0840	85	1	1	-1	6.8998	24	0	1	1	6.7404	87	1	1	0
6.5780	104	1	-2	0	6.4167	39	1	-1	1	6.3987	8	0	2	0
5.9285	35	1	0	1	5.5612	13	1	-2	1	5.3957	81	2	-1	-1
5.3243	270	2	0	-1M	5.3243	270	2	-1	0M	5.2854	92	1	0	-2
5.0946	84	0	1	-2M	5.0946	84	1	1	-2M	5.0345	40	1	2	-1
4.9592	30	2	0	0	4.9106	80	0	0	2	4.8721	66	2	-2	0
4.7752	39	0	2	1	4.7022	136	1	-1	-2	4.6768	47	2	-2	-1
4.6591	46	1	2	0	4.5754	52	0	2	-2	4.5529	39	2	1	-1
4.4520	11	2	0	-2	4.3969	3	0	3	-1	4.3605	9	1	-3	1
4.2658	54	0	3	0	4.2019	60	0	1	2	4.1899	127	2	-1	1
4.1247	47	1	-1	2	4.0430	135	2	-3	0	4.0067	4	1	-2	2
3.9546	4	1	-3	-1	3.8671	1	1	-2	-2	3.7997	7	0	3	-2M
3.7997	7	2	-3	-1M	3.7784	60	2	-2	-2	3.7479	12	1	3	-1
3.7394	42	3	-1	-1	3.6884	25	2	2	-1	3.6813	10	2	-3	1
3.6003	999	3	-2	-1	3.5799	27	1	-3	2+	3.5597	14	0	3	1
3.5418	26	1	0	-3	3.5273	12	3	-1	0	3.5184	30	1	3	-2
3.4850	13	1	3	0	3.4499	24	0	2	2	3.4287	20	1	-4	1
3.4211	52	3	0	-2	3.4136	62	0	1	-3	3.4010	12	2	0	-3
3.3702	11	2	2	0	3.3632	40	1	1	2M	3.3632	40	1	2	-3M
3.3523	38	2	1	1	3.3345	5	0	4	-1	3.3252	9	2	1	-3
3.2890	4	2	-4	0	3.2737	11	0	0	3	3.2483	43	2	-1	-3+
3.2084	17	2	-2	2	3.1993	11	0	4	0	3.1723	14	2	-1	2
3.1670	27	3	1	-2	3.0721	14	1	-4	2	3.0552	19	2	-3	2
3.0503	8	0	3	-3	3.0008	16	2	3	-1M	3.0008	16	1	3	-3M
2.9749	57	1	-2	3+	2.9589	49	1	3	1	2.9469	16	1	4	-1+
2.8844	15	1	4	-2	2.8477	6	2	2	1	2.8442	11	0	3	2
2.8377	30	1	-3	3	2.8279	4	3	-4	-1	2.8150	12	0	4	1
2.8035	14	1	0	3	2.7851	31	4	-2	-1M	2.7851	31	4	-1	-1M
2.7730	20	2	3	0	2.7654	18	3	-2	-3M	2.7654	18	1	4	0M
2.7243	66	4	-1	-2	2.7306	4	1	-5	0	2.7105	6	2	-5	0M
2.7105	6	3	-4	1M	2.7054	18	0	4	-3	2.6966	92	4	-2	-2M
2.6966	92	1	1	-4M	2.6692	5	0	5	-1	2.6629	34	4	-3	-1+
2.6351	22	1	2	-4	2.6161	4	1	-5	2	2.6030	16	1	-4	3
2.5923	82	0	5	-2	2.5781	8	3	2	0M	2.5781	8	3	-4	-2M
2.5594	77	0	5	0M	2.5594	77	1	1	3M	2.5479	20	4	-3	-2M
2.5479	20	0	2	-4M	2.5271	9	3	-3	2	2.5189	6	3	-3	-3
2.5139	3	1	-3	-3	2.4956	9	2	4	-1+	2.4817	12	2	-1	3+
2.4779	3	1	-1	-4	2.4594	11	4	-4	-1	2.4554	6	4	1	-1
2.4507	39	0	3	-4M	2.4507	39	4	-2	-3M	2.4447	10	3	-5	-1
2.4264	7	2	3	1	2.4175	9	3	3	-1	2.4124	5	1	5	-2
2.3858	19	2	4	-3	2.3689	12	2	3	-4	2.3613	11	3	3	-3
2.3539	5	3	0	2	2.3511	6	2	-2	-4	2.3359	3	1	-5	3M

2.3359	3	0	5	1	2.2878	29	0	4	-4+	2.2846	28	1	5	0M
2.2846	28	4	1	0M	2.2744	7	1	5	-3M	2.2744	7	3	2	1M
2.2533	8	3	-4	-3M	2.2533	8	3	-5	-2M	2.2321	7	4	-5	0M
2.2321	7	5	-2	-1M	2.2263	7	3	-5	2M	2.2263	7	4	0	-4M
2.2195	9	4	-1	-4+	2.2137	5	4	2	-3	2.2083	6	1	-5	-2
2.1986	5	5	-1	-1M	2.1986	5	0	6	-2M	2.1685	14	2	1	3
2.1651	7	2	-6	-1	2.1595	4	2	4	-4M	2.1595	4	3	3	-4M
2.1521	6	3	4	-2+	2.1488	9	4	-2	-2	2.1327	8	0	6	0M
2.1327	8	4	-5	1M	2.1196	11	2	5	-1	2.1111	15	1	4	2
2.1049	6	3	4	-3	2.1010	6	3	4	-1	2.0915	11	2	4	1
2.0831	6	2	3	2M	2.0831	6	3	-4	3M	2.0782	13	5	-1	0
2.0625	10	1	5	-4	2.0603	11	5	-4	-2	2.0538	13	5	-4	0M
2.0538	13	4	-4	2M	2.0485	21	0	2	-5	2.0426	3	1	6	-1
2.0368	18	1	-5	4	2.0347	10	4	-1	2	2.0301	10	0	1	-5
2.0215	4	4	-6	0	2.0186	19	0	4	3M	2.0186	19	3	2	-5M
1.9666	5	2	-6	3	1.9938	10	4	3	-1	1.9732	35	5	-5	1M
1.9732	35	5	-1	-4M	1.9620	10	1	4	-5	1.9485	11	5	-5	0M
1.9485	11	4	0	-5M	1.9447	11	1	6	0	1.9391	6	5	-4	-3
1.9281	12	5	-4	1M	1.9281	12	1	-7	0M	1.9154	5	3	-7	1
1.9117	6	2	4	-5	1.8998	6	0	6	-4M	1.8998	6	4	-6	-2M
1.8972	4	0	7	-1	1.8902	4	1	2	4	1.8758	12	4	2	1M
1.8758	12	1	-6	4M	1.8707	5	2	-7	-1	1.8678	7	1	-1	5
1.8618	6	3	-7	-1	1.8530	8	6	-3	-2	1.8471	13	1	-4	5M
1.8471	13	6	-1	-2M	1.8442	9	6	-3	-1	1.8407	6	4	-6	2
1.8359	11	2	6	-1	1.8327	9	5	2	-1M	1.8327	9	1	5	-5M
1.8302	5	0	5	-5	1.8274	15	6	-2	-3	1.8218	6	3	-3	4
1.8198	14	6	-1	-3	1.8183	6	4	-4	3	1.7999	24	6	-4	-2+
1.7912	10	2	3	3M	1.7912	10	1	7	-2M	1.7838	4	3	3	2
1.7745	11	4	-3	-5M	1.7745	11	6	-3	0M	1.7706	7	2	-6	-3
1.7570	4	1	7	-3	1.7474	9	5	1	-5M	1.7474	9	3	-7	-2M
1.7440	13	6	0	-1	1.7366	6	2	-3	5	1.7253	4	5	2	0
1.7196	3	0	7	-4	1.7087	5	4	-7	2	1.7073	8	0	6	-5
1.6957	4	6	-3	-4	1.6626	4	4	2	-6	1.6483	8	5	-6	2
1.6421	5	2	7	-3	1.6250	4	4	-2	-6	1.6177	4	0	3	5
1.6162	4	6	2	-3	1.6073	6	1	-3	6	1.6063	10	6	2	-2
1.5959	6	5	4	-2	1.5934	7	3	1	4	1.5925	9	4	-7	3
1.5496	6	7	-4	-3	1.5436	7	2	1	5M	1.5436	7	2	7	0M
1.5319	5	6	-4	2	1.5144	7	1	8	-4	1.4587	5	1	1	6
1.4466	4	6	3	-5										

Acknowledgements

Use of the Advanced Photon Source at Argonne National Laboratory was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. ICDD is thanked for the partial support through the Grants-in-Aid program.

Synchrotron X-ray Investigation of α -Chlorohemin, $C_{34}H_{32}ClFeN_4O_4$, an Fe-porphyrin

J.A, Kaduk, W. Wong-Ng, L.P. Cook, B. Chakraborty, S.H. Lapidus, L. Ribaud, G. Brewer

(1a)

(1b)

Fig. 2

Fig. 3

Fig. 4

(a)

(b)

Fig. 6