

tance we found the same value of 3.4 Å. Most angles show but small deviations from the tetrahedral angle 109°; only the angle between the bonds C<sub>1</sub>-C<sub>2</sub> and C<sub>2</sub>-C<sub>3</sub> amounts to 123° (see Table 4).

Table 4. *Interbond angles*

(Calculated for the parameter values of Table 3.)

C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> = 123°	C <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub> = 113°
Cl <sub>2</sub> -C <sub>2</sub> -C <sub>1</sub> = 109°	Cl <sub>5</sub> -C <sub>5</sub> -C <sub>4</sub> = 112°
Cl <sub>2</sub> -C <sub>2</sub> -C <sub>3</sub> = 107°	Cl <sub>5</sub> -C <sub>5</sub> -C <sub>6</sub> = 108°
C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub> = 105°	C <sub>5</sub> -C <sub>6</sub> -C <sub>1</sub> = 107°
Cl <sub>3</sub> -C <sub>3</sub> -C <sub>2</sub> = 112°	Cl <sub>6</sub> -C <sub>6</sub> -C <sub>5</sub> = 114°
Cl <sub>3</sub> -C <sub>3</sub> -C <sub>4</sub> = 103°	Cl <sub>6</sub> -C <sub>6</sub> -C <sub>1</sub> = 104°
C <sub>3</sub> -C <sub>4</sub> -C <sub>5</sub> = 117°	C <sub>6</sub> -C <sub>1</sub> -C <sub>2</sub> = 107°
Cl <sub>4</sub> -C <sub>4</sub> -C <sub>3</sub> = 116°	Cl <sub>1</sub> -C <sub>1</sub> -C <sub>6</sub> = 114°
Cl <sub>4</sub> -C <sub>4</sub> -C <sub>5</sub> = 115°	Cl <sub>1</sub> -C <sub>1</sub> -C <sub>2</sub> = 111°

**Optical data**

By means of the Federow method we measured the orientation of the polarization ellipsoid. Refractive indices were measured by immersion methods. We found:

$$n_{\alpha} = 1.62; n_{\beta} = 1.64; n_{\gamma} = 1.67.$$

$$\text{Optical axial angle} = 60^{\circ}.$$

Optic sign +.

$$n_{\gamma} = b; \angle(a, n_{\alpha}) = 107^{\circ}; \angle(a, n_{\beta}) = 17^{\circ}; \angle(c, n_{\alpha}) = 15^{\circ}; \angle(c, n_{\beta}) = 75^{\circ}.$$

We express our thanks to Dr v. d. Laan, who kindly put samples of some C<sub>6</sub>H<sub>6</sub>Cl<sub>6</sub> isomers at our disposal.

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**Patterson and Fourier Projections of Single Molecules of Haemoglobin**

BY KATE DORNBERGER-SCHIFF

*Institut für Medizin und Biologie, Berlin-Buch, Germany*

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The one-dimensional Patterson synthesis and several one-dimensional Fourier syntheses of a single molecule of haemoglobin are computed on the basis of X-ray data published by Perutz. Conclusions on the shape of the molecule are drawn from the Fourier projections, and modifications of Perutz's model of the molecule are suggested.

It is a well-known fact that proteins, if they crystallize at all, do so with varying amounts of water and that the unit-cell dimensions depend on the amount. It has so far been generally assumed (see, for example, Crowfoot (1938), Bernal & Fankuchen (1941), Boyes-Watson, Davidson & Perutz (1947), Bernal & Carlisle (1948)) that in the wet crystals the protein molecules are separated from each other throughout by layers of water. To explain the perfect arrangement of the molecules in these crystals it was then necessary (Bernal & Fankuchen, 1941) to assume long-range forces acting between the molecules. However, these assumptions are not necessary unless it is taken for granted that each molecule lies completely within the boundaries of one unit cell, in the dry crystal. Short-range forces may be responsible for the order in wet crystals as well, if each molecule stretches through two or more unit cells of the dry crystal (see below). This seems more satisfactory in view of the striking fact that the molecules must be much better aligned in wet than in dry crystals,

as the former give far better photographs than the latter.

Following these considerations, it was thought promising to concentrate first on the shape of the protein molecule. Elsewhere (Dornberger-Schiff, 1949) the principle of a method has been outlined for the calculation of the Patterson function or the electron density of *single molecules* from the observed intensities or structure factors of different crystals of the same substance with varying water content. This method can therefore be used to give the shape of the molecule and thus to decide about the necessity of assuming long-range forces; sufficient data were available to apply it to haemoglobin and to yield Fourier and Patterson projections of a single molecule on to a line parallel to the *c'* axis (normal to *a* and *b*). (The full details of the method used are to be described in another paper.)

Only the intensities and *F* values of the (00*l*) reflexions of the crystals in different states of swelling and shrinkage were required, for, as Boyes-Watson *et al.*

(1947) have shown conclusively, the molecules form solid layers parallel to the  $a$  and  $b$  axes, which remain unaltered when the haemoglobin crystal swells or shrinks. The resulting curves will give the Patterson

assumed by Perutz to be nodal points and the one point on which he was doubtful (marked in Fig. 9 of his paper by an arrow). Thus we can distinguish five regions, separated from each other by possible nodal points; in

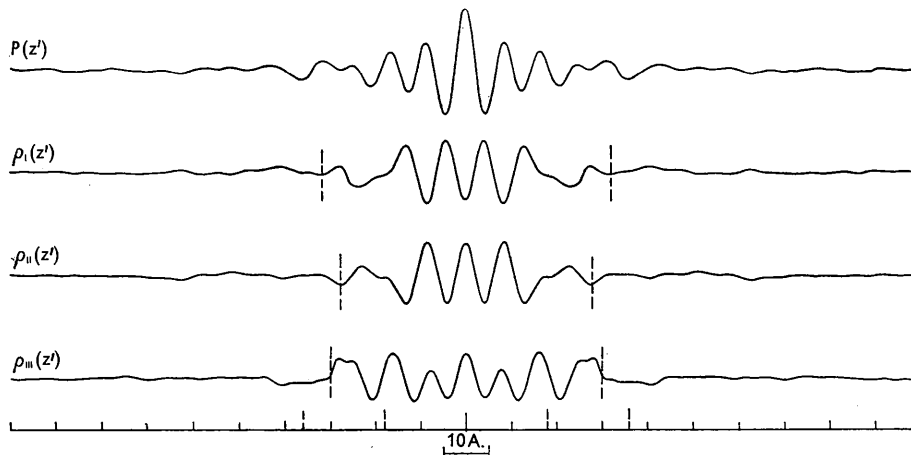


Fig. 1. One-dimensional projections relating to single haemoglobin molecules.  $P(z')$ , Patterson projection;  $\rho_I(z')$ ,  $\rho_{II}(z')$  and  $\rho_{III}(z')$ , Fourier projections with different assumptions of signs. Broken lines indicate the assumed or derived breadth of the molecule.

and density distribution of a single molecule, embedded entirely in a sea of water. We therefore expect the curves to show constant values  $\rho(z') = \rho_{\text{water}}$  and  $P(z') = P_{\text{water}}$  respectively, outside the region on to which the molecule itself or its Patterson synthesis projects; inside this region clearly recognizable maxima and minima may occur. Thus the molecule must extend at least as far as the region of 'hills and valleys' but may extend even further. The results of the calculations, which were based on the data published by Boyes-Watson *et al.* (1947, Table 8, p. 118), are shown in Fig. 1.

The projection on  $c'$  of Perutz's cylindrical model of the haemoglobin molecule is 36 A. in extent; the projection of the Patterson is therefore 72 A. Thus the verdict of the Patterson projection ( $P(z')$ , Fig. 1) is not conclusive and it was decided to calculate Fourier projections as well.

The first step was to take the signs for the  $F$  values deduced by Perutz on the basis of his cylindrical model. The resulting curve ( $\rho_I(z')$ , Fig. 1) indicates a projection of the molecule at least about 64 A. in extent and is thus in contradiction to the model from which it was deduced.

Next an attempt was made to arrive at as complete a survey as possible of all density distributions compatible with the observed intensity data. For that purpose the intensities  $I_{00l}$  were plotted against  $\sin \theta/\lambda$  (Boyes-Watson *et al.* 1947, Fig. 9, p. 118) (giving in effect a plot of the square of the Fourier transform in reciprocal space). We then have to keep in mind that the Fourier transform may only change its sign where its square touches the zero line. It seems extremely unlikely to do so except at four points: the three points

each of them the Fourier transform possesses a constant sign. But as the change of signs at these points may or may not occur, we cannot tell the signs of the

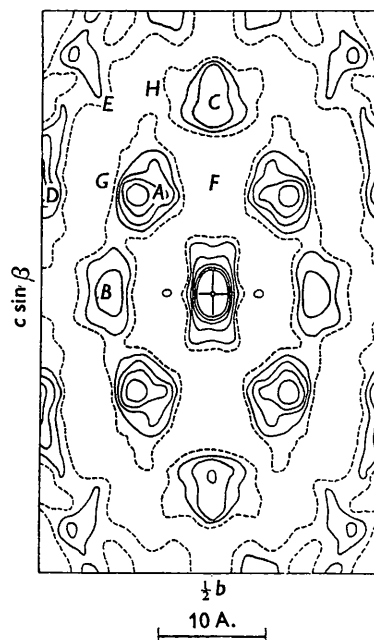


Fig. 2. Patterson projection on  $b, c'$  plane of normal wet haemoglobin (taken from Boyes-Watson *et al.* 1947). The capital letters refer to the vectors correspondingly marked in Fig. 3. (Reproduced, by kind permission, from *Proceedings of the Royal Society.*)

different regions. All  $2^5 = 32$  combinations of signs were therefore in turn used as basis for the Fourier synthesis and the corresponding curves were plotted. All of them

showed outside a certain region constant values which could be interpreted as corresponding to the embedding water of the molecule; this region, however, was in no case as narrow as 36 Å., as would have to be expected for the cylindrical model.

The curve with the smallest region of 'hills and valleys' is the curve  $\rho_{II}(z')$  (Fig. 1), still indicating an extension of the molecule of about 56 Å. It has minima at the apparent boundaries of the molecule which do not seem easy to explain.

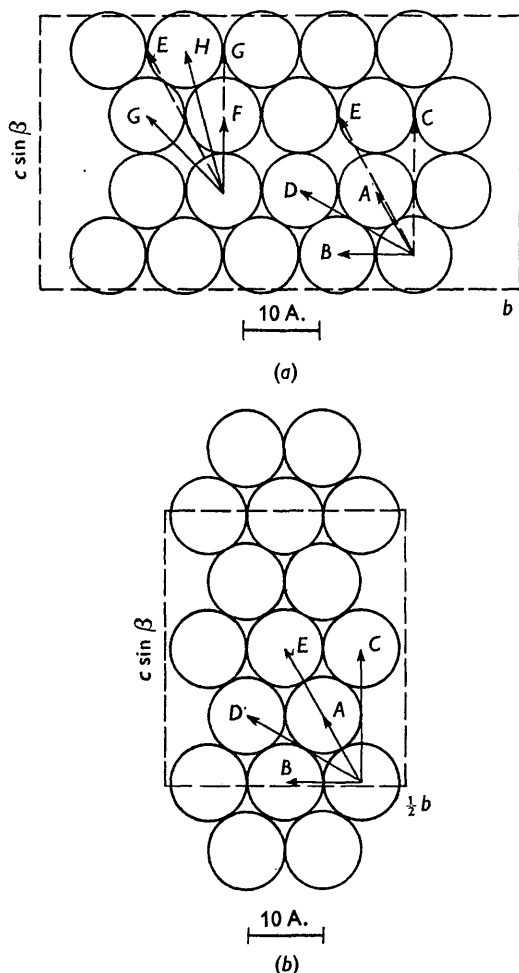


Fig. 3. Cross-section parallel to  $b, c'$  through haemoglobin molecule (a) according to Perutz (1949), (b) with an odd number of layers. The vectors correspond to the points in the Patterson projection (Fig. 2) marked in a similar way.

$\rho_{III}(z')$  is another of the thirty-two curves which seems to me rather more likely to be the representation of the electron density than any other of them (except perhaps one differing from it only in minor details) because of the clear distinction between the protein region and the pure-water region. It leads to an extension of the molecule of about 60 Å. and seven equidistant maxima, the outer ones being broadened.

Perutz (1949), in his second paper on haemoglobin, has proposed a type of structure the main feature of

which he based on a detailed discussion of the three-dimensional Patterson synthesis: the structure is built up of layers, about 8 Å. apart and parallel to the  $a, b$  plane, consisting of polypeptide chains parallel to the  $a$  axis at distances about 10 Å. apart. Minor details of his type of structure, however, were undoubtedly chosen to comply with the cylindrical model and its con-

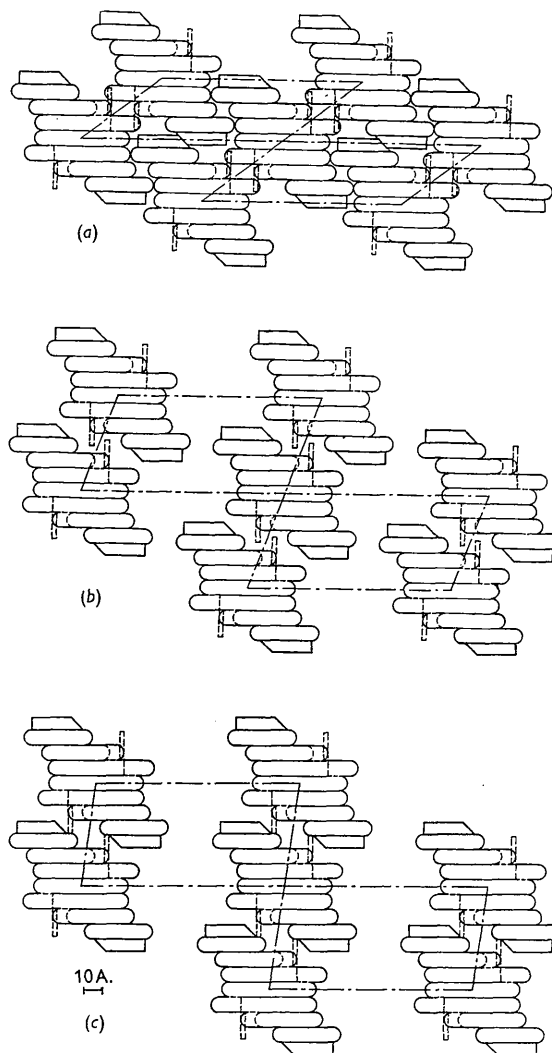


Fig. 4. Possible cross-section parallel to  $a, c$  through haemoglobin crystals: (a) dry crystal (unit cell no. 10); (b) normal wet crystal (no. 5); (c) expanded crystal (no. 6). Another possible cross-section is shown in broken lines.

sequences, especially the four layers of chains. An improvement on this type of structure seems possible by the assumption of an uneven number of layers. This can be seen by comparing the maxima of the Patterson projection on the  $b, c$  plane obtained by Perutz (Boyes-Watson *et al.* 1947, Fig. 3 (a), p. 98; Perutz, 1949, Fig. 21, p. 485), reproduced in Fig. 2, with the vectors between the projections on this plane of the main chains in the case of an even (Fig. 3 (a)) or uneven (Fig. 3 (b)) number of layers. Whereas the arrangement according

to Fig. 3 (a) would account only for the maxima *A*, *B* and *D*, but leave *C* and *E* unexplained, all these maxima would be expected on assuming a type of structure shown in Fig. 3 (b). On the other hand, no unobserved maxima could be derived on that basis, whereas Fig. 3 (a) would demand maxima *F*, *G* and *H*.

The existence of seven layers seems more likely than of five, for in the latter case the side chains or haem groups would have to be responsible for the extension of the molecule in the *c'* direction being at least 56 Å. instead of about 42 Å.—the width of the five layers. The outline of the model represented by Fig. 4 is actually based on the assumption of seven layers.

It is possible to tackle the problem of the shape of the molecule from a different angle, starting from the above-mentioned hypothesis that short-range forces are keeping the molecules in position in the crystals at all states of swelling or shrinkage. The experimental data to be explained on this basis are the varying lattice constants of the dry, partly wet, wet and expanded crystals, as measured by Boyes-Watson *et al.* (1947, Tables 1 and 3, p. 93). They would be consistent with a cross-section of the molecule like the one shown in Fig. 4 in the arrangements it would assume in the dry,

normal wet, and expanded crystal. But this is not the only model consistent with these data. It should only serve as an example which seems preferable to all models suggested up to the present, in so far as it would be in keeping with (i) the one-dimensional Fourier projection (on *c'*) of the molecule, (ii) the Patterson projection (on the *b, c* plane) of the normal wet crystal, and (iii) the lattice constants of the various stages of swelling and shrinkage explained on the basis of short-range forces only. Further experimental data will have to be used to reject or confirm the outline of this model and, perhaps, to refine it.

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## The Crystal Structure of Hollandite, the Related Manganese Oxide Minerals, and $\alpha$ - $\text{MnO}_2$

BY ANDERS BYSTRÖM AND ANN MARIE BYSTRÖM

*Institute of General and Physical Chemistry, University of Stockholm, and Geological Survey of Sweden, Stockholm 50, Sweden*

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Hollandite, cryptomelane, coronadite and  $\alpha$ - $\text{MnO}_2$  form an isostructural series of the general formula  $A_{2-y}B_{8-z}X_{16}$ , *A* being large ions such as  $\text{Ba}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{K}^+$ , *B* small and medium-sized ions such as  $\text{Mn}^{4+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ , and *X* in the cases investigated  $\text{O}^{2-}$  and  $\text{OH}^-$  ions. The unit cell, which contains one formula unit, is tetragonal or pseudotetragonal, in the latter case monoclinic. Approximate dimensions of the tetragonal unit cell are  $a = 9.8$  and  $c = 2.86$  Å. When deformed the short axis will be the *b* axis of the monoclinic cell. The deviation of  $\beta$  from  $90^\circ$  is  $0.5\text{--}1.5^\circ$ , and the difference  $a - c$  is  $0.1\text{--}0.2$  Å. The space group of the tetragonal cell is  $C_{4h}^2\text{--}I4/m$  and the atomic positions are

$$\begin{aligned} (0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + & \quad 2-y \text{ } A \text{ in } 2(b): \quad 0, 0, \frac{1}{2}; \\ & \quad 8-z \text{ } B \text{ in } 8(h): \quad x_1, y_1, 0; \bar{x}_1, \bar{y}_1, 0; \bar{y}_1, x_1, 0; y_1, \bar{x}_1, 0; \\ & \quad 8 \text{ } X \text{ in } 8(h): \quad \begin{cases} x_2, y_2, 0; \text{ etc.;} \\ x_3, y_3, 0; \text{ etc.} \end{cases} \end{aligned}$$

For a hollandite specimen the parameters were calculated to be

$$\begin{aligned} x_1 = 0.348, \quad x_2 = 0.153, \quad x_3 = 0.542, \\ y_1 = 0.167, \quad y_2 = 0.180, \quad y_3 = 0.167. \end{aligned}$$

The *A* ion is surrounded by eight oxygen ions at a distance of 2.74 Å. forming a cube and at a greater distance (3.31 Å.) by four oxygen ions forming a square at the same *z* level as the *A* ion. The *B* ion is surrounded by six oxygen ions forming an octahedron, and with a mean distance of  $B\text{--}O = 1.98$  Å.

In the cases investigated, the variable *y* in the general formula varies from 0.8 to 1.3 and *z* from 0.1 to 0.5.

### 1. Introduction

In the course of a study of manganese oxides, precipitates consisting of  $\alpha$ - $\text{MnO}_2$  were obtained by the

reduction of a  $\text{KMnO}_4$  solution by various reagents, for instance,  $\text{H}_2\text{O}_2$  and  $\text{HCl}$ . As has been stated previously (Cole, Wadsley & Walkley, 1947), and as we could con-