The Crystal and Molecular Structure of Dihydroxo(1,2,3,4,5,6,7,8-octaethyl-porphinato)antimony(V) Perchlorate Monoethanol Solvate: a Crystal Structure that Exhibits a Subcell

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The crystal structure of dihydroxo(1,2,3,4,5,6,7,8-octaethylporphinato)antimony(V) perchlorate monoethanol solvate has been determined from the intensities of 6988 unique reflections measured with an automated diffractometer. The compound crystallizes in space group $P2_1/n$ with $a = 15\cdot848$ (2), $b = 23\cdot370$ (2), $c = 10\cdot717$ (2) Å, and $\beta = 92\cdot12$ (1)°. The distribution of intensities indicates a subcell with parameters $a/2$, b, c and β but the space group for the subcell is $P2_1/c$. The reflections with $h = 2n$ have an average intensity 10·6 times that of the $h = 2n + 1$ data. Infinite columns of hydrogen-bonding running through the crystal, $\cdots HO-porphyrin-OH \cdots perchlorate \cdots ethanol \cdots HO-porphyrin-OH \cdots$, require that the perchlorate anion and the ethanol solvate exist in a pseudocentrosymmetric relation. This pseudosymmetry, to which the existence of the subcell is related, is partially responsible for the distorted octahedral geometry exhibited by the Sb complex. The porphyrin ring is approximately planar with a maximum deviation from the least-squares plane of 0·08 Å with the Sb atom essentially in the plane. The ethyl group of the ethanol solvate is disordered such that the methyl group occupies two positions with equal probability. The structure was refined by full-matrix least-squares techniques to a conventional R value of 0·043 for the 4923 reflections greater than $2\sigma(I)$.

Introduction

The porphyrin macrocycle has been found to form stable, crystalline complexes with Mg, Sn, Tl, many of the transition metals and, more recently, As, Sb and Bi. The crystal structure of the title compound is of interest for a variety of reasons. The three-dimensional structure of this compound could aid the interpretation of the spectral work currently in progress on this class of compounds (Sayer, Gouterman & Connell, 1977; Connell, 1976) since the identity of the axial ligands was in doubt when work on the crystal structure was started. It was evident from the quality of the crystals that a precise model for a Group V*a* metal–porphyrin complex would result from a careful structure analysis. Details of the porphyrin ring ruffling, the degree of planarity of Sb and the four pyrrole N atoms and to what extent this structure does or does not display 'tenting' (Cullen & Meyer, 1974) can be established with certainty only on the basis of a precise model. In addition, the distribution of intensities clearly indicated the existence of a subcell, making the structure of distinct crystallographic interest.

Experimental

Crystals of dihydroxo(1,2,3,4,5,6,7,8-octaethylporphinato)antimony(V) perchlorate monoethanol solvate (SbOEP hereinafter) were prepared by Dr Phillip Sayer, Department of Chemistry, University of Washington. The crystals were grown by dissolving the salt in a minimum of hot, 95% ethanol. Ether was added dropwise to the refluxing solution until saturation was reached, then the sealed flask was placed in a Dewar containing hot water. After three days the long, red, needle-shaped crystals were harvested. Some decomposition of the complex occurs at reflux temperature, as evidenced by a white residue. The crystals are parallelepipeds elongated in the **a** direction and bounded by {100}, {010}, and {001}.

The diffraction pattern exhibited monoclinic symmetry, conforming to space group $P2_1/n$ (equivalent positions x,y,z; $\bar{x},\bar{y},\bar{z}$; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$) based on the systematic absences $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$. Table 1 summarizes the crystal data.

Reflections with $h = 2n + 1$ are weak, indicating the presence of a subcell with translation $a/2$. Note that *on the basis of subcell reflections only*, ignoring the $h = 2n + 1$ data and reindexing so that h' (the index for the subcell) equals $h/2$, the space group would be designated $P2_1/c$.

Intensity data were collected in three shells on a computer-controlled, four-circle diffractometer to a 2θ limit of 50° (Nb-filtered Mo $K\alpha$ radiation, $\lambda = 0\cdot71069$ Å). A crystal, 0·66 × 0·12 × 0·30 mm, mounted with the long dimension approximately parallel to the φ axis,

Table 1. *Crystal data*

Dihydroxo(octaethylporphinato)antimony(V)   perchlorate   ethanol solvate $[C_{16}H_{44}N_4Sb^V(OH)_2]^+(ClO_4)^-(CH_3CH_2OH)$

Space group $P2_1/n$

$a = 15.848(2)$ Å	$M_r = 834.06$
$b = 23.370(2)$	$\mu = 8.272$ cm^{-1}
$c = 10.717(2)$	$(\sin\theta_{max})/\lambda = 0.595$
$\beta = 92.12(1)°$	$F(000) = 1728$
$V = 3966.5$ Å^3	$d_o = 1.38(1)$ g cm^{-3}
$Z = 4$ molecules/unit cell	$d_c = 1.397$

was used for data collection. The first shell of data was collected with a scan range of $1.0°$ plus the separation due to the $\alpha_1-\alpha_2$ splitting and backgrounds were counted for 20 s at each end of the scan. The scan width was increased to $1.2°$ plus the $\alpha_1-\alpha_2$ separation for the outer two shells. The larger reflections were remeasured at reduced current and coincidence corrections were applied. Nine standard reflections were observed at varying intervals throughout the data collection with no indication of crystal deterioration. All work was done at room temperature ($t = 21 \pm 2°C$).

6988 unique reflections were collected of which 4923 were greater than $2\sigma_I$ $[\sigma_I^2 = P_1 + (B_1 + B_2)(T_S/2T_B)^2 + (kP)^2$ where P_1, B_1 and B_2 are the peak and background counts, T_S and T_B are the scan and individual background counting times and k was set at 0.025 based on variations in individual monitor reflections]. The data were corrected for absorption with an analytical absorption correction program (Templeton & Templeton, 1973) and appropriate Lorentz and polarization corrections were made while the data were reduced in the usual way. The scattering factor curves and anomalous scattering terms for all atoms except H were taken from *International Tables for X-ray Crystallography* (1974); all atoms were assumed to be in the zero ionization state. The H scattering factors of Stewart, Davidson & Simpson (1965) were used.

Structure solution and refinement

The initial work on the structure was based on the subcell reflections only. Structure factors calculated for Sb at the special position (in the subcell) $0.5,0,0.5$ gave a residual $R (= \Sigma || F_o | - | F_c ||/\Sigma | F_o |)$ of 0.44. An F_o synthesis along with ΔF syntheses revealed the porphyrin ring system, the axial ligands bound to Sb, a solvent molecule (thought to be water at this point) and electron density interpreted to be a perchlorate ion with an occupancy of 0.5. This model with 28 atoms (isotropic temperature factors) refined by least-squares techniques to $R = 0.115$ based on 3505 subcell reflections with $I > 2\sigma(I)$.

In transforming this model to the $P2_1/n$ unit cell one must decide which of two possible models is correct.

One of these would require two half-Sb atoms lying on different centers of symmetry and the asymmetric unit would consist of two half-molecules. The alternative model would allow a single Sb atom at the general position $0.25,0,0.5$ and the asymmetric unit would consist of one whole molecule. In one pass of least-squares refinement of the two half-molecules model (isotropic thermal parameters) R decreased from 0.424 to 0.302. Refinement of the whole-molecule model in the same manner reduced R from 0.342 to 0.207. The latter model clearly fits the data better, although one of the two half-occupied perchlorate ions was obviously incorrect.

A Patterson synthesis with only reflections for which $h = 2n + 1$ had maxima that corresponded to the coordinates of the perchlorate ion and the solvent molecule. Nothing else of significance could be obtained from this Patterson function, which is essentially an indication of the difference between the two halves of the true unit cell.

Two cycles of isotropic refinement followed by F_o syntheses indicated that the perchlorate ion occurred only in a single site. The supposed water of hydration was then required to occur in the single site that is pseudocentrosymmetrically related to the perchlorate ion site. This model reduced R to 0.177.

Refinement of the model with anisotropic thermal parameters was carried out in blocks. At an intermediate step in the refinement ($R = 0.118$), an F_o synthesis showed that the model was incomplete in the area of the solvent of hydration. Two additional C atoms were added to the model assuming that the solvent molecule was ethanol, although there was a possibility that the solvent was a disordered ether molecule.

After every atom in the model had been refined at least once with anisotropic thermal parameters ($R = 0.065$), a difference synthesis showed the positions of all 44 H atoms of the porphyrin and the three hydroxyl H atoms in the structure. The solvent molecule was seen to be a disordered ethanol and the H atoms bound to the disordered ethyl group were not located at this point. Five more passes refining the anisotropic model in blocks of 15 atoms per pass reduced R to 0.045 with unit weights and holding the H atom parameters fixed. The H atom parameters were varied in one additional pass with all others fixed, reducing R to 0.043. A difference synthesis then revealed concentrations of electron density at the anticipated sites for six of the ten H atoms of the disordered ethanol molecule. Since the ethyl group is best described as a single α-C atom with two 0.5 occupied β-C atoms, the H atoms were expected to be present at no more than 0.5 occupancy. The observed positions were adjusted to give apparent C—H bond distances of 1.0 Å and the additional four positions were calculated.

Further refinement of the anisotropic model was carried out with statistical weights $[w_F = 1/(\sigma_F)^2]$ while

holding the H atom parameters fixed. The model was divided into three blocks for the final stages of refinement; the first block contained Sb, the hydroxyl O atoms, the perchlorate anion and the disordered ethanol; the second block included Sb and 21 atoms of the porphyrin macrocycle; and the third block consisted of Sb and 21 atoms of the porphyrin macrocycle. The scale factor was adjusted in every block.

The refinement was considered complete after three passes on the first block and two passes on each of the other two. The maximum shift over error in the final passes was 0·90 with an average shift over error of 0·10. The conventional R was 0·043, the weighted residual, R_w ($= \Sigma w \| F_o | - | F_c \| / \Sigma w | F_o |$), was 0·046 and $R_{F^2} = 0·053$ for the 4923 reflections greater than $2\sigma_I$. R for all data is 0·060 and the goodness of fit is 2·03. This value reflects, in part, the underestimation of the e.s.d.'s as might be expected from partitioning the parameters into three separate matrices and, in part,

limitations of the model for the perchlorate anion and the disordered ethanol molecule.

At the conclusion of the refinement a ΔF synthesis was calculated. Electron density of peak height $\pm 0·7$ e Å^{-3} was found in the location of the perchlorate anion. The difference map in the area of the porphyrin ring system contained no significant electron density.

Results

The bond distances and angles and the numbering of the atoms are shown in Fig. 1. C—C distances have not been corrected for the effects of thermal shortening. The average C—H bond distance in the porphyrin moiety is 0·98 (9) Å. Individual C—H bond lengths varied from 0·77 to 1·20 Å. Angles associated with the H atoms were within statistical limits of the expected values. H atom positions associated with the disordered
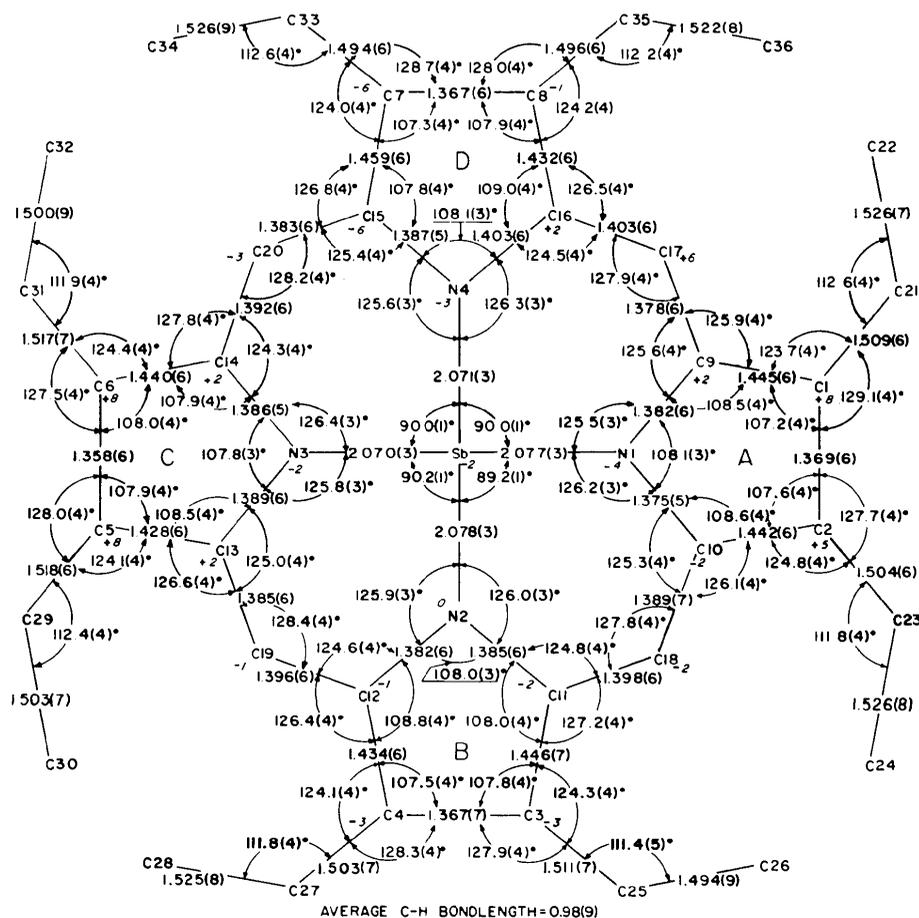
Fig. 1. Bond lengths, in Å, angles, in degrees, and deviations of the porphyrin ring from the best least-squares plane (italicized numerals), in Å × 10⁻³.
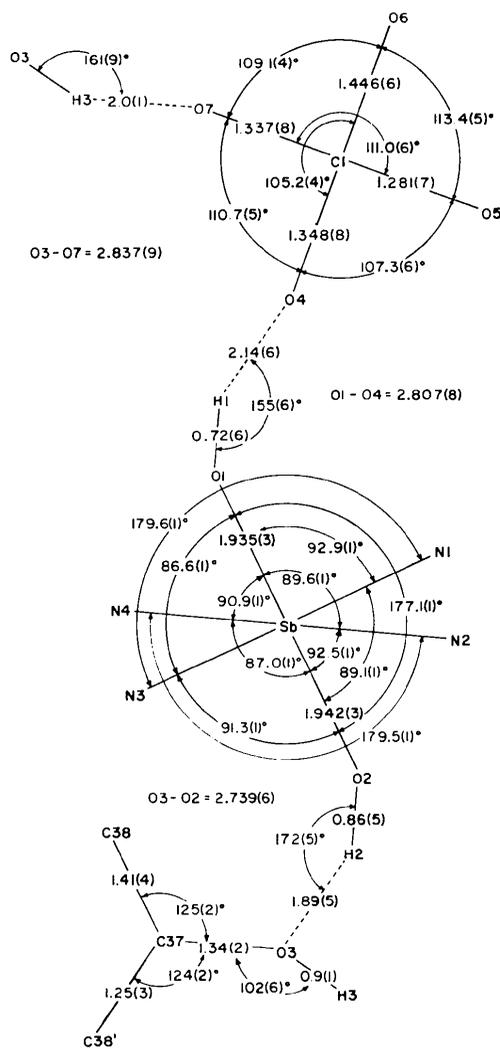
Fig. 1 (cont.)

ethyl group of the ethanol solvate were calculated: C–H bond lengths were restricted to 1·0 Å and tetrahedral coordination was assumed.

Fig. 1 also illustrates the deviations of individual atoms from the least-squares plane of the porphyrin ring. Fig. 2 is a stereoscopic *ORTEP* plot (Johnson, 1965) of the asymmetric unit. A stereoscopic view illustrating the hydrogen-bonding scheme and the unit-cell contents is shown in Fig. 3. Table 2 contains the atom positions and thermal parameters.* Table 3 contains averaged values for several parameters in this and two related structures. Table 4 tabulates the angle between the individual pyrrole rings illustrating the low degree of ruffling that occurs in this structure.

Discussion

Subcell

The existence of the subcell is primarily related to the perchlorate ion and the disordered ethanol molecule. In Fig. 4, *A* and *B* represent sites occupied by the perchlorate anion and the disordered ethanol respectively, as they are found in the structure. If the pseudo-centers in Fig. 4 were true centers, thus halving the unit cell along **a**, sites *A* and *B* would be identical. The existence of the subcell is due to the nonidentity of sites *A* and *B*.

The difference in scattering power of the two groups occupying sites *A* and *B* combined with the deviation from a centrosymmetric relation accounts for most of

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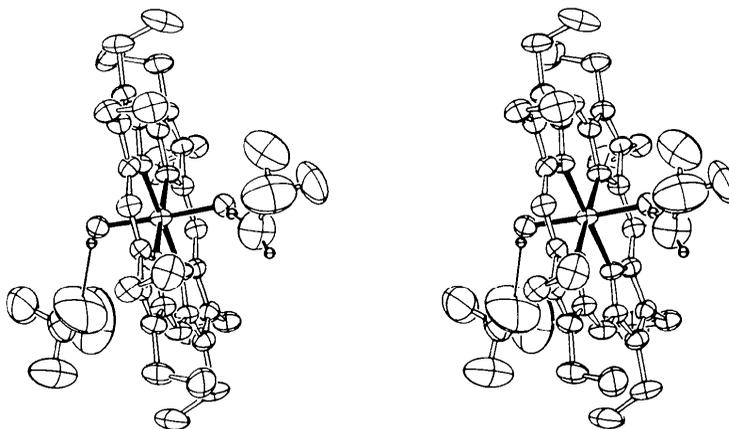
Fig. 2. Stereoscopic view of the asymmetric unit. The hydrogen atoms involved in hydrogen-bonding are included and have been assigned isotropic *B* values of 1·0 for clarity. Hydrogen atoms bound to carbon have not been included.
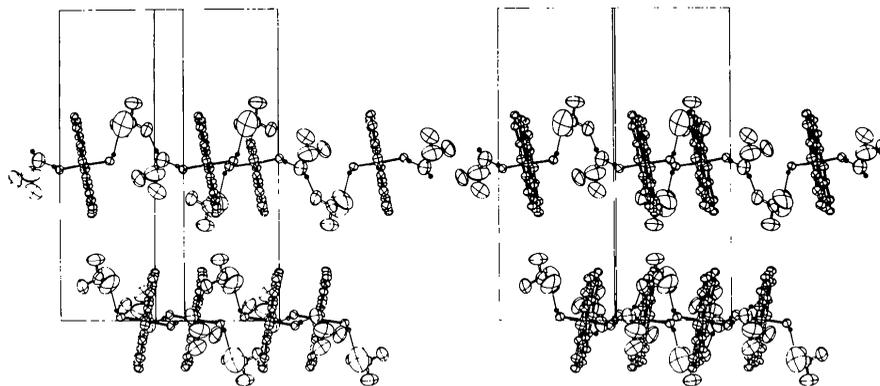
Fig. 3. Stereoscopic view of the contents of two unit cells illustrating packing and hydrogen-bonding in the crystal. The view is approximately along the [101] vector. Only hydrogen atoms involved in hydrogen-bonding have been included and the ethyl groups on the porphyrin have also been deleted for clarity.

Table 2. *Atomic parameters*

Thermal parameters for the heavy atoms are defined by the expression

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

Values of U_{ij} have been multiplied by 10^2. For hydrogen atoms the thermal parameter is defined by $\exp(-8\pi^2U^2\sin^2\theta/\lambda^2)$. The value of U has been multiplied by 10^2.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb	0·25295 (2)	−0·00158 (1)	0·49159 (2)	3·80 (1)	2·84 (1)	3·72 (2)	−0·09 (1)	0·92 (1)	−0·15 (1)
Cl	0·2510 (1)	0·13625 (8)	0·1133 (2)	8·3 (1)	9·8 (1)	7·4 (1)	−0·1 (1)	0·15 (9)	2·2 (1)
O(1)	0·1887 (2)	0·0102 (1)	0·3367 (3)	5·4 (2)	4·7 (2)	4·8 (2)	−0·5 (2)	0·2 (1)	0·6 (2)
O(2)	0·3175 (2)	−0·0176 (1)	0·6451 (3)	4·6 (2)	5·0 (2)	3·9 (2)	0·5 (1)	0·2 (1)	0·1 (1)
O(3)	0·2475 (4)	0·0129 (2)	0·8652 (4)	15·4 (5)	12·9 (5)	7·3 (3)	0·6 (4)	3·3 (3)	−1·9 (3)
O(4)	0·2212 (5)	0·1151 (3)	0·2201 (7)	30 (1)	22·0 (8)	22·4 (8)	−2·4 (7)	6·6 (7)	14·7 (7)
C(5)	0·3310 (4)	0·1284 (4)	0·1170 (9)	9·0 (5)	46 (2)	33 (1)	10·1 (7)	0·7 (6)	−9 (1)
O(6)	0·2271 (4)	0·1960 (2)	0·1120 (5)	23·2 (7)	8·2 (4)	16·2 (5)	1·7 (4)	4·8 (5)	0·3 (4)
O(7)	0·2145 (6)	0·1102 (3)	0·0141 (7)	45 (1)	13·4 (6)	21·8 (8)	11·6 (7)	−22·2 (9)	−8·6 (5)
N(1)	0·3335 (2)	0·0664 (1)	0·4584 (3)	4·1 (2)	3·1 (2)	4·3 (2)	−0·5 (2)	1·2 (2)	−0·2 (2)
N(2)	0·1720 (2)	0·0537 (2)	0·5810 (3)	4·2 (2)	3·6 (2)	4·6 (2)	−0·0 (2)	1·2 (2)	−0·2 (2)
N(3)	0·1723 (2)	−0·0693 (1)	0·5233 (3)	4·5 (2)	3·5 (2)	4·1 (2)	−0·3 (2)	1·2 (2)	0·2 (2)
N(4)	0·3344 (2)	−0·0565 (1)	0·4037 (3)	4·4 (2)	3·1 (2)	4·1 (2)	−0·1 (2)	1·3 (2)	−0·3 (2)
C(1)	0·4499 (3)	0·1183 (2)	0·4063 (4)	4·6 (3)	3·7 (3)	3·7 (2)	−0·7 (2)	0·2 (2)	0·2 (2)
C(2)	0·3951 (3)	0·1550 (2)	0·4614 (4)	5·5 (3)	3·7 (3)	3·7 (2)	−1·1 (2)	0·5 (2)	0·0 (2)
C(3)	0·1112 (3)	0·1342 (2)	0·6594 (4)	5·7 (3)	4·1 (3)	5·4 (3)	0·9 (2)	1·3 (3)	−0·6 (2)
C(4)	0·0580 (3)	0·0895 (2)	0·6802 (4)	4·6 (3)	4·7 (3)	4·5 (3)	0·9 (2)	0·9 (2)	−0·2 (2)
C(5)	0·0626 (3)	−0·1224 (2)	0·5933 (4)	4·4 (3)	4·4 (3)	4·3 (3)	−0·5 (2)	0·9 (2)	0·3 (2)
C(6)	0·1158 (3)	−0·1589 (2)	0·5367 (4)	4·8 (3)	3·6 (3)	4·6 (3)	−0·9 (2)	0·7 (2)	0·2 (2)
C(7)	0·3936 (3)	−0·1368 (2)	0·3194 (4)	4·5 (3)	3·7 (3)	4·5 (3)	0·5 (2)	0·7 (2)	−0·5 (2)
C(8)	0·4480 (3)	−0·0923 (2)	0·3034 (4)	4·3 (3)	3·6 (3)	3·9 (2)	0·5 (2)	0·7 (2)	−0·4 (2)
C(9)	0·4111 (3)	0·0623 (2)	0·4046 (4)	4·5 (3)	3·8 (3)	3·3 (3)	−0·5 (2)	0·7 (2)	0·1 (2)
C(10)	0·3221 (3)	0·1223 (2)	0·4945 (4)	5·1 (3)	3·3 (3)	4·3 (3)	−0·4 (2)	1·0 (2)	−0·2 (2)
C(11)	0·1833 (3)	0·1121 (2)	0·5963 (4)	4·7 (3)	3·5 (3)	4·8 (3)	−0·2 (2)	1·0 (2)	−0·1 (2)
C(12)	0·0959 (3)	0·0390 (2)	0·6309 (4)	3·8 (3)	4·1 (3)	4·2 (3)	0·2 (2)	0·8 (2)	−0·1 (2)
C(13)	0·0971 (3)	−0·0661 (2)	0·5855 (4)	3·7 (3)	4·3 (3)	4·1 (3)	−0·5 (2)	0·5 (2)	−0·2 (2)
C(14)	0·1852 (3)	−0·1260 (2)	0·4917 (4)	4·4 (3)	3·4 (3)	4·3 (3)	0·0 (2)	0·7 (2)	0·1 (2)
C(15)	0·3215 (3)	−0·1146 (2)	0·3846 (4)	4·7 (3)	3·1 (2)	4·0 (3)	0·6 (2)	0·7 (2)	−0·1 (2)
C(16)	0·4115 (3)	−0·0423 (2)	0·3567 (4)	3·8 (3)	3·7 (3)	3·6 (2)	−0·2 (2)	0·8 (2)	−0·1 (2)
C(17)	0·4463 (3)	0·0129 (2)	0·3594 (4)	4·0 (2)	4·1 (3)	3·9 (2)	−0·2 (2)	1·1 (2)	−0·1 (2)
C(18)	0·2531 (3)	0·1429 (2)	0·5569 (4)	6·4 (3)	3·0 (3)	5·0 (3)	−0·1 (2)	1·4 (2)	−0·5 (2)
C(19)	0·0624 (3)	−0·0163 (2)	0·6312 (4)	3·9 (3)	4·7 (3)	4·7 (3)	−0·2 (2)	1·0 (2)	−1·0 (2)
C(20)	0·2536 (3)	−0·1456 (2)	0·4259 (4)	5·2 (3)	2·9 (2)	5·1 (3)	−0·1 (2)	1·0 (2)	−0·2 (2)
C(21)	0·5353 (3)	0·1306 (2)	0·3547 (4)	5·2 (3)	3·8 (3)	5·8 (3)	−0·9 (2)	1·2 (2)	0·4 (2)
C(22)	0·5313 (4)	0·1392 (3)	0·2135 (5)	7·5 (4)	10·1 (5)	5·8 (4)	−1·2 (4)	2·2 (3)	0·4 (3)
C(23)	0·4059 (3)	0·2182 (2)	0·4828 (5)	7·3 (4)	3·3 (3)	8·0 (4)	−1·2 (3)	2·1 (3)	−0·5 (3)
C(24)	0·3728 (5)	0·2531 (3)	0·3710 (7)	13·2 (6)	4·3 (4)	12·1 (6)	0·2 (4)	−1·2 (5)	1·2 (4)
C(25)	0·0993 (3)	0·1965 (2)	0·6929 (5)	6·5 (4)	5·1 (3)	8·1 (4)	1·6 (3)	2·0 (3)	−1·2 (3)

Table 2 (cont.)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(26)	0·1212(5)	0·2072(3)	0·8276(7)	12·2(6)	7·7(5)	13·4(6)	3·9(4)	−3·9(5)	−5·1(5)
C(27)	−0·0234(3)	0·0899(2)	0·7477(5)	4·4(3)	6·3(4)	6·5(3)	0·5(3)	1·6(3)	−1·3(3)
C(28)	−0·0113(4)	0·0682(3)	0·8814(5)	8·5(5)	14·0(6)	6·0(4)	−0·8(4)	2·9(3)	−0·2(4)
C(29)	−0·0173(3)	−0·1368(2)	0·6605(5)	4·8(3)	5·4(3)	6·4(3)	−1·7(3)	1·7(3)	−0·2(3)
C(30)	−0·0021(4)	−0·1422(3)	0·7992(5)	9·2(5)	10·6(5)	6·1(4)	−1·5(4)	3·0(3)	0·5(4)
C(31)	0·1085(3)	−0·2235(2)	0·5269(5)	6·1(3)	3·8(3)	8·8(4)	−1·3(3)	2·1(3)	−0·5(3)
C(32)	0·1465(5)	−0·2529(3)	0·6400(7)	14·6(7)	5·6(4)	11·2(5)	2·7(4)	3·7(5)	2·9(4)
C(33)	0·4014(3)	−0·1974(2)	0·2768(5)	5·6(3)	3·7(3)	·7·8(4)	0·2(2)	1·6(3)	−1·2(3)
C(34)	0·3638(4)	−0·2067(3)	0·1451(7)	10·1(5)	7·5(5)	12·6(6)	1·4(4)	−2·1(4)	−6·4(4)
C(35)	0·5303(3)	−0·0928(2)	0·2395(5)	4·5(3)	4·9(3)	6·4(3)	0·4(2)	1·1(2)	−0·6(3)
C(36)	0·5220(4)	−0·0694(3)	0·1070(5)	8·2(4)	14·9(7)	5·3(4)	−1·1(4)	3·1(3)	−0·7(4)
C(37)	0·230(1)	−0·0284(7)	0·947(2)	31(2)	15(1)	19(1)	−3(1)	12(1)	2(1)
C(38)	0·237(1)	−0·088(1)	0·924(3)	9(1)	25(3)	23(3)	2(2)	3(2)	13(2)
C(38')	0·280(2)	−0·046(1)	1·031(3)	17(2)	19(3)	23(3)	7(2)	−12(2)	2(2)

	x	y	z	U		x	y	z	U
H(1)	0·203(4)	0·031(2)	0·293(5)	8(2)	H(C30)1	0·036(5)	−0·170(4)	0·822(7)	15(3)
H(2)	0·291(3)	−0·007(2)	0·710(5)	9(1)	H(C30)2	0·023(5)	−0·106(4)	0·847(7)	11(3)
H(3)	0·250(6)	0·043(4)	0·912(9)	15(4)	H(C30)3	−0·047(5)	−0·151(4)	0·848(7)	13(3)
H(C17)	0·500(3)	0·016(2)	0·329(5)	5(1)	H(C31)1	0·139(4)	−0·235(3)	0·471(6)	8(2)
H(C18)	0·252(4)	0·186(2)	0·579(5)	6(2)	H(C31)2	0·047(4)	−0·232(3)	0·501(6)	9(2)
H(C19)	0·009(4)	−0·020(2)	0·672(5)	5(2)	H(C32)1	0·118(5)	−0·244(4)	0·721(7)	16(3)
H(C20)	0·251(3)	−0·183(2)	0·410(5)	6(2)	H(C32)2	0·151(5)	−0·286(4)	0·639(8)	17(3)
H(C21)1	0·555(4)	0·166(3)	0·394(5)	6(2)	H(C32)3	0·213(5)	−0·244(4)	0·626(8)	15(3)
H(C21)2	0·575(4)	0·100(3)	0·378(5)	6(2)	H(C33)1	0·376(4)	−0·225(3)	0·336(6)	8(2)
H(C22)1	0·512(5)	0·104(3)	0·174(7)	10(2)	H(C33)2	0·458(4)	−0·209(3)	0·284(6)	8(2)
H(C22)2	0·493(5)	0·173(3)	0·191(7)	11(2)	H(C34)1	0·314(5)	−0·194(4)	0·150(7)	11(3)
H(C22)3	0·588(5)	0·147(3)	0·190(7)	10(2)	H(C34)2	0·407(5)	−0·190(4)	0·093(7)	12(3)
H(C23)1	0·374(4)	0·264(3)	0·504(6)	20(2)	H(C34)3	0·363(5)	−0·249(4)	0·126(7)	10(3)
H(C23)2	0·466(4)	0·229(3)	0·496(6)	11(2)	H(C35)1	0·554(4)	−0·127(3)	0·246(6)	6(2)
H(C24)1	0·312(5)	0·237(4)	0·311(7)	16(3)	H(C35)2	0·571(4)	−0·070(3)	0·290(6)	6(2)
H(C24)2	0·381(5)	0·288(4)	0·388(8)	13(3)	H(C36)1	0·508(5)	−0·025(4)	0·110(7)	17(3)
H(C24)3	0·404(6)	0·247(4)	0·294(8)	17(3)	H(C36)2	0·487(5)	−0·100(4)	0·055(7)	9(3)
H(C25)1	0·136(4)	0·226(3)	0·650(6)	9(2)	H(C36)3	0·562(5)	−0·076(4)	0·066(7)	11(3)
H(C25)2	0·050(4)	0·209(3)	0·679(6)	12(2)	H(C37)1	0·26	−0·02	1·03	22·80
H(C26)1	0·081(6)	0·207(4)	0·879(8)	25(3)	H(C37)2	0·17	−0·02	0·98	22·80
H(C26)2	0·128(6)	0·248(4)	0·848(8)	16(3)	H(C37)3	0·17	−0·02	0·98	22·80
H(C26)3	0·182(5)	0·192(4)	0·852(8)	13(3)	H(C37)4	0·20	−0·06	0·90	22·80
H(C27)1	−0·068(4)	0·068(3)	0·695(6)	7(2)	H(C38)1	0·29	−0·10	0·89	19·00
H(C27)2	−0·055(4)	0·127(3)	0·748(6)	13(2)	H(C38)2	0·21	−0·10	0·84	19·00
H(C28)1	0·036(5)	0·093(4)	0·937(7)	14(3)	H(C38)3	0·22	−0·12	0·98	19·00
H(C28)2	−0·062(5)	0·075(4)	0·928(8)	13(3)	H(C38')1	0·31	−0·01	1·08	20·26
H(C28)3	−0·010(5)	0·030(4)	0·895(7)	16(3)	H(C38')2	0·34	−0·05	1·00	20·26
H(C29)1	−0·047(4)	−0·172(3)	0·619(6)	9(2)	H(C38')3	0·27	−0·08	1·09	20·26
H(C29)2	−0·066(4)	−0·109(3)	0·637(6)	9(2)					

the intensity in the $h = 2n + 1$ data. The average intensity of the $h = 2n$ data is 10·6 times that of the $h = 2n + 1$ data. In addition, one can conclude that had Sb truly been on a center (the two half-molecules model), there would be no subcell exhibited since the ethanol molecule and the perchlorate ion sites would both be equally occupied by both the ethanol molecule and the perchlorate ion. The a axis would have been halved and the space group would be $P2_1/c$.

Metal–porphyrin complex

Metal–porphyrin complexes may exhibit ruffling (Meyer, 1972; Cullen & Meyer, 1974), folding (Koenig, 1965) and 'tenting' (Pettersen, 1969; Cullen & Meyer, 1974) depending on the size of the metal atom, the type of coordination exhibited by the metal atom, and the

environment in which the complex exists. The SbOEP structure may be compared to two tin–porphyrin complex structures from the literature, $\alpha,\beta,\gamma,\delta$-tetraphenyl-porphinatodichlorotin(IV)   (Cl$_2$SnOEP)   (Collins, Scheidt & Hoard, 1972) and octaethylporphinato-dichlorotin(IV) (Cl$_2$SnOEP) (Cullen & Meyer, 1973). The metal ion and the porphyrin ring are coplanar in all three structures. Table 3 contains some averaged bond lengths and angles for the two Sn–porphyrin complexes and the SbOEP complex. The two OEP complexes are very similar to one another, and distances involving Sb and the size of the 'hole' in the macrocycle are the only ones that possibly differ significantly.

Although the porphyrin ring system is expected to be planar on resonance grounds, the SbOEP structure exhibits ruffling. The metal–porphyrin complex is pseudo-centrosymmetric about the metal ion, as is indicated by

variations in the ruffling of the ring system. This variation is due to the asymmetric environment in which the porphyrin complex is packed. There is no folding of the porphyrin ring in this structure (see Fig. 1).

Distortions from planarity, such as the ruffling observed with SbOEP, may be attributed to packing forces in the crystal. Such forces are unlikely to alter significantly chemically equivalent bonds and angles in the porphyrin ring system. The averaged values for the various distances and angles shown in Table 3 are, therefore, better estimates of the true values than any one of the experimentally observed values. The basis of the statistical treatment of the data must be considered when trying to ascertain if a quantity determined in one structure is different from an equivalent quantity in another structure. SbOEP appears to differ signifi-

cantly from Cl$_2$SnTPP in distances involving the metal atom and the size of the 'hole' in the ring system. Most of the distances and angles involving the sites of substitution C(b) and C(m) are different in a statistical sense (see below) in the two structures.

The C(a)—C(m)—C(a) angles in Cl$_2$SnOEP and SbOEP differ by 1·4°. On a statistical basis this difference is significant. Furthermore, the C(a)—C(m)—C(a) angles in the two OEP complexes differ significantly from the corresponding angle in Cl$_2$SnTPP.

The C(b)—C(b) distances (1·365, 1·368 Å) in the two OEP complexes are shorter than the C(b)—C(b) distance in the TPP complex (1·380 Å). Also, the C(a)—C(m) distances (1·390, 1·386 Å) in the OEP complexes appear to be different from the C(a)—C(m) distance observed in the Cl$_2$SnTPP structure just at the level of the significance. Variation of C(b)—C(b) bond lengths with (sin θ)/λ of the data set has been discussed (Collins, Scheidt & Hoard, 1972; Hoard, 1975) and the systematic error introduced by using only low-angle data appears to be substantial. The C(b)—C(b) bond length in Cl$_2$SnTPP was found to be 1·366 (3) Å in the refinement procedure utilizing the full data set, a statistical weighting scheme, appropriate corrections for absorption, and including H atom contributions. A similar variation in bond length with (sin θ)/λ has been observed with thiocytosine (Furberg & Jensen, 1970). With these results in mind one cannot conclude that the C(b)—C(b) bond lengths in the two OEP structures are significantly different from the C(b)—C(b) distances observed in the Cl$_2$SnTPP structure. The C(a)—C(m) distances are not affected to the extent that the C(b)—C(b) distances are by the use of low-angle data (Collins, Scheidt & Hoard, 1972) and, therefore, one concludes that the distances and angles involving C(m) are significantly different when comparing SbOEP to Cl$_2$SnTPP.

The M—C(a) distances do not differ significantly in

Table 3. *Averaged bond lengths (Å) and angles (°) for three related metalloporphyrin complexes*

	^{a}[(OH)$_2$Sb^{V}OEP]$^+$	^{b}Cl$_2$Sn^{IV}OEP	^{c}Cl$_2$Sn^{IV}TPP
M—OH	1·938 (4)^d	–	–
M—Cl	–	2·453 (2)^d	2·420 (1)^d
M—N	2·074 (2)	2·082 (1)	2·098 (2)
M—C(m)	3·440 (2)	3·424 (8)	3·469 (2)
N—C(a)	1·383 (2)	1·379 (3)	1·370 (1)
C(a)—C(m)	1·390 (3)	1·386 (5)	1·407 (1)
C(a)—C(b)	1·441 (3)	1·437 (6)	1·446 (1)
C(b)—C(b)	1·365 (2)	1·368 (4)	1·380 (3)
N—N	2·933 (2)	2·944 (2)	2·967 (2)
X—M—N^e	90·0 (8)	90·1 (1)	90·0
N—M—N	90·0 (1)	90·0 (1)	90·0
M—N—C(a)	126·0 (1)	125·9 (2)	125·4 (1)
C(a)—N—C(a)	108·0 (1)	108·2 (2)	109·2 (2)
N—C(a)—C(b)	108·4 (2)	108·3 (4)	108·2 (1)
N—C(a)—C(m)	124·9 (2)	124·4 (2)	126·4 (1)
C(b)—C(a)—C(m)	126·7 (2)	127·3 (2)	125·4 (1)
C(a)—C(b)—C(b)	107·7 (1)	107·6 (1)	107·2 (1)
C(a)—C(m)—C(a)	128·1 (1)	129·5 (4)	126·3 (2)

Notes: (a) This work. (b) Cullen & Meyer (1973). (c) Collins, Scheidt & Hoard (1972). Note that the C(b)—C(b) distance of 1·380 (3) Å was observed when high-angle data only were used in the refinement. The value observed with the complete data set was 1·363 (3) Å. (d) Values in parentheses are the standard deviations of the mean as defined by Hamilton (1964) except where only one value of the quantity is available, in which case the experimental standard deviation is used. (e) X = OH in (OH)$_2$Sb^V OEP, Cl in Cl$_2$Sn^{IV}OEP and in Cl$_2$Sn^{IV}TPP. (f) For purposes of discussion the unique atoms of the porphyrin ring system have been

$$\begin{array}{c} \text{C}(b)\text{—C}(b) \\ \nearrow \qquad \searrow \end{array}$$

designated C(a), C(b) and C(m) as shown: C(a)   C(a)—C(m).
$$\searrow_{\text{N}} \nearrow$$
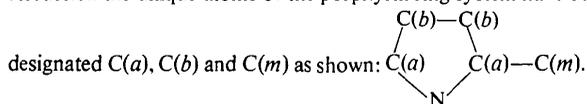
Table 4. *Ruffling angles in the porphyrin ring (°)*

Pyrrole rings involved		Angle between rings
A	B	2·97
B	C	2·56
C	D	4·57
D	A	1·65
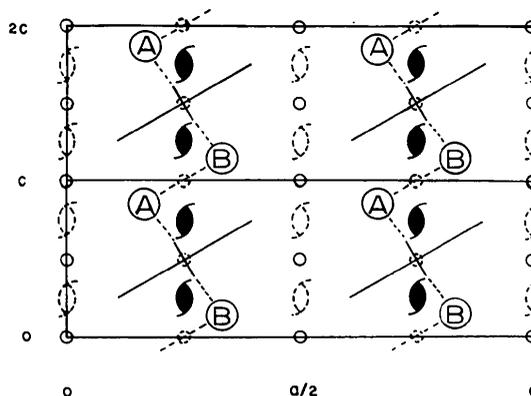
Fig. 4. Representation of the symmetry elements present in the $P2_1/n$ unit cell as viewed down **b**. Elements of pseudosymmetry which are present are indicated by dashed lines.

the three complexes; 3·100 Å in Cl₂SnTPP, 3·099 Å in Cl₂SnOEP and 3·096 Å in SbOEP.

The Sb—O bond lengths (1·935, 1·942 Å) in this structure are shorter than previously observed values of 2·048 Å (Brun & Brändén, 1966), 2·185 Å (Ferguson & Hawley, 1974) and 1·985 Å (Ferguson & Ridley, 1973). Approach to Sb in the previously reported structures is much more hindered than is the approach to the planar Sb–porphyrin complex. The observed value (1·94 Å) is expected to be more representative of a normal Sb—O bond distance than are the values from those determined in more hindered systems.

The Sb—N distances in this structure are restricted by the porphyrin ring system and may be quite different from the expected value in an Sb complex with a unidentate ligand. Other Sb—N distances previously reported are 2·236 Å (Ferguson & Ridley, 1973) and 2·281 Å (Patton & Raymond, 1969).

The Sb–porphyrin complex exists in an asymmetric environment as a result of the perchlorate–ethanol relation. The variation in ruffling around the porphyrin ring is largely due to this asymmetry. Table 4 lists the ruffling angles between the individual pyrrole rings.

The coordination geometries of previously determined Sb structures have included both distorted trigonal bipyramidal and distorted octahedral complexes. The Sb–porphyrin complex exhibits distorted octahedral geometry. The N—M—O angles vary from 86·6 to 92·9° and the O—M—O angle is 177·1°. It appears that the perchlorate ion crowds O(1) to the extent that it is tilted away from the normal to the porphyrin ring. Likewise, the disordered ethanol molecule apparently crowds O(2) away from a strictly perpendicular position. The amount of crowding seems to be related to the hydrogen-bonding scheme (Fig. 4) and to the packing in the crystal structure.

The perchlorate ion

The dimensions of the perchlorate ion agree reasonably well with previously reported values (Kass & Sørensen, 1973; Wright & Quinn, 1974). The thermal parameters are substantially higher than many previously reported, which probably accounts for the short average Cl—O distance of 1·36 Å with a standard deviation of 0·06 Å. The average O—Cl—O angle is 109·5° with a standard deviation of 1·2°.

The ethanol molecule

The ethanol molecule occupies a volume of space in the crystal which is approximately the same size as the perchlorate ion. The model of the ethyl group is disordered and the atoms all have large thermal parameters. The O(3)—H(3) bond length [0·9 (1) Å] is reasonable for this type of bond (Hamilton & Ibers, 1968, p. 52). A hydrogen bond is formed between H(3) and O(7) of

a perchlorate in an adjacent asymmetric unit. In addition, H(2) forms a hydrogen bond to O(3). The hydrogen bonding tends to anchor the hydroxyl end of the ethanol molecule. The C(37)—O(3) bond length [1·34 (2) Å] is considerably shorter than the expected value of 1·424 Å (Liminga, 1967) but this is not surprising in view of the thermal motion of C(37). Likewise, the C(37)—C(38) and C(37)—C(38′) distances [1·41 (4), 1·25 (3) Å] also appear to be affected by the disorder and thermal motion.

Crystal structure and hydrogen-bonding

The hydrogen-bonding scheme observed in this crystal structure, while relatively simple, is an essential part of the structure. The ribbons or columns of hydrogen-bonding running through the crystal parallel to c (see Fig. 4) are responsible for the $P2_1/n$–$P2_1/c$ subcell relation. Each ribbon has a directional sense and its four nearest neighbors have the opposite sense. This arrangement of the ribbons allows minimal electrostatic repulsions to occur between pairs of perchlorate anions and thus is an energetically favorable situation.

The ethanol molecule is anchored into a hole that is large enough to allow disordering of the ethyl group at full occupancy. All H atoms available to form hydrogen bonds do so in this structure.

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Redetermination of the Structure of β-Dicalcium Silicate

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The structure of β-Ca$_2$SiO$_4$ [first determined by Midgley, *Acta Cryst.* (1952), 5, 307–312] has been redetermined on the basis of three-dimensional diffractometer data. In spite of a systematic error in indexing in the original work, the new result confirms the principles of the previous determination. In the second part of the paper a hypothesis on the structural background of hydraulic activity of calcium silicates is discussed. High coordination of Ca by Ca, low mean Ca—Ca distances within these polyhedra and the sharing of faces of neighbouring CaO$_x$ polyhedra seem to be characteristic features of hydraulically active compounds.

Introduction

The structure of β-Ca$_2$SiO$_4$ was determined more than 20 years ago by Midgley (1952) from $hk0$, $h0l$ and $0kl$ data within the limits of the Cu sphere. The structure was later refined by Cruickshank (1964) with the same set of intensity data. In the results the strong distortion of the SiO$_4$ tetrahedron is particularly striking. Therefore, and because β-Ca$_2$SiO$_4$ is now the only Portland cement mineral whose structure is not known accurately,* we have examined it with new experimental data. An error in indexing – all hkl and $hk\bar{l}$ were interchanged – was found to be the reason why Midgley could not obtain a reliable result. That the main features of the former structure are correct, in spite of this error, is due to the relatively small deviation of the monoclinic angle in β-Ca$_2$SiO$_4$ from 90°.

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* The structure of an alite remains unknown but Golovastikov, Matveyeva & Belov (1975) have determined the structure of pure tricalcium silicate, Ca$_3$O(SiO$_4$) = Ca$_3$SiO$_5$.

Crystallographic data and intensity measurement

Crystallographic and intensity measurement data are in Tables 1 and 2.

In the measurement of the intensities it had to be taken into account that the $hk0$ reflexions of both twin orientations obscure one another and, because of the lattice dimensions, the reflexions $hk,10$ and 11 are in the immediate neighbourhood of $h + 1,k,10$ and 11 re-

Table 1. *Crystallographic data*

Substance:	β-Dicalcium silicate, grown at 1300°C from a CaCl$_2$ melt without addition of stabilizing reagents
Symmetry:	Monoclinic, space group $P2_1/n(C^5_{2h})$
Cell parameters:	$a = 5.502 \pm 0.001$; $b = 6.745 \pm 0.001$; $c = 9.297 \pm 0.001$ Å; $\beta = 94.59 \pm 0.02°$ $V = 343.9$ Å^3; $Z = 4$; $D_x = 3.326$ g cm^{-3} at 20°C
Remarks:	All crystals twinned on (100)