SHORT STRUCTURAL PAPERS

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Lead Phthalocyanine

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Abstract. Monoclinic, $P2_1/b$, $a=25{\cdot}48$ (8), $b=25{\cdot}48$ (8), $c=3{\cdot}73$ (1) Å, $\gamma=90°$, $PbC_{32}N_8H_{16}$, $Z=4$, $D_x=1{\cdot}98$ g cm^{-3}. The non-planar molecule of lead phthalocyanine stacks linearly, to form a molecular column parallel to the c axis.

Introduction. Lead phthalocyanine (abbreviated as PbPc) was prepared by the reaction of PbO and phthalonitrile in refluxing α-chloronaphthalene (Kroenke & Kenney, 1964). Dark purple needle-shaped crystals were grown by sublimation at about 250°C in a stream of nitrogen at 5 to 7 torr. The crystal data were obtained from oscillation, Weissenberg and precession photographs about the long axis of the crystal, and powder diagrams calibrated with silver powder. The reflexions consist of two types: sharp and strong ones, and diffuse and weak ones. Intensities of 349 $hk0$–$hk3$ independent sharp reflexions (out of 773 accessible reflexions) were estimated by the visual method from multiple-film equi-inclination Weissenberg photographs using Ni-filtered Cu $K\alpha$ radiation. The sample used to collect the intensity data was roughly a cylinder with a mean diameter of 0·065 mm. The observed intensities were corrected for Lorentz and polarization factors and absorption correction was also applied assuming the crystal to be a cylinder ($\mu=139$ cm^{-1}). As far as the sharp reflexions are concerned, the crystal lattice is tetragonal with Laue symmetry $4/m$. These sharp reflexions define a subcell within the true cell by the matrix given below:

$$\begin{pmatrix} h' \\ k' \\ l' \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

At the initial stage the crystal structure was deduced based on sharp reflexions only and finally determined taking the diffuse reflexions into account. The systematic absences of the sharp reflexions ($h'+k'+l'=2n+1$) are consistent with a body-centered tetragonal lattice. By heavy-atom methods, the difference Fourier syntheses were calculated and yielded the approximate atomic coordinates of the non-hydrogen atoms. The atomic coordinates, temperature factors and four layer scale factors were refined by the full-matrix least-squares method with unit weight for the sharp reflexions. During this process hydrogen atoms were placed at calculated positions assuming the C–H distance to be 1·08 Å, but these were not refined. Atomic scattering factors for Pb, C, N and H, as well as the real and imaginary anomalous dispersion correction for a lead atom were obtained from *International Tables for X-ray Crystallography* (1962). The final R value for sharp reflexions was 0·057.* The shuttlecock-shaped molecule stacks linearly, to form a molecular column parallel to the c axis as shown in Fig. 1. The crystal structure consists of a square array of these molecular columns. The remaining degree of freedom is the sense of the fourfold axis of the molecule with regard to the c axis, because the intensities of sharp reflexions are insensitive to this. There are three possible arrangements of the molecular columns in the crystal arising

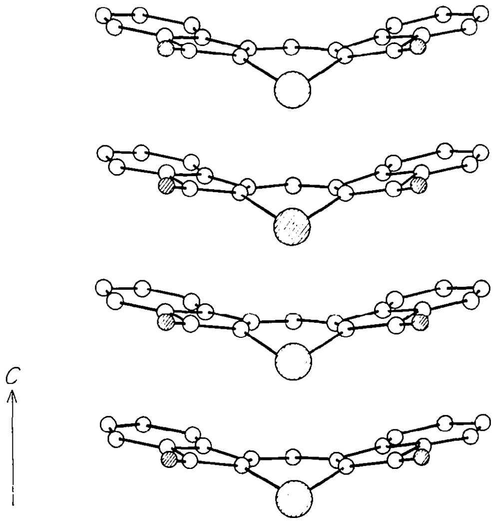

Fig. 1. The molecular column of PbPc.

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* A list of observed and calculated structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30156 (4 pp.). Copies can be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

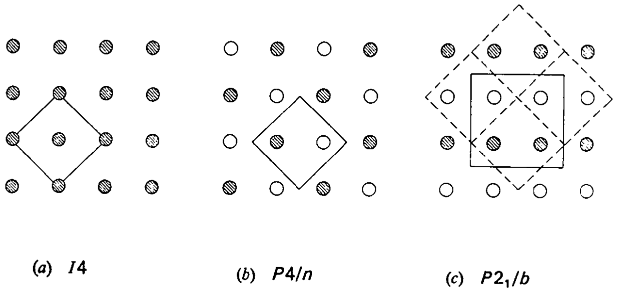
from the sense of the fourfold axis of the molecule (Fig. 2):

(*a*) all molecular columns have the same sense;

(*b*) the nearest-neighbour columns have the opposite sense;

(*c*) the next-nearest-neighbour columns have the opposite sense.

Diffuse reflexions are those with $h'=n+\frac{1}{2}$ and $k'=n+\frac{1}{2}$; this implies that the true structure is the superstructure with double cell dimensions, namely, the arrangement (*c*) as shown in Fig. 2. The final positional parameters, their e.s.d.'s and the corresponding thermal parameters are given in Table 1.



(*a*) *I*4 (*b*) *P*4/*n* (*c*) *P*2₁/*b*

Fig. 2. The three possible arrangements of the molecular columns. A cross-hatched circle represents the molecular column with the upward molecules and an open circle that with the downward molecules, respectively. A solid line shows a unit cell and a dashed line a subcell.

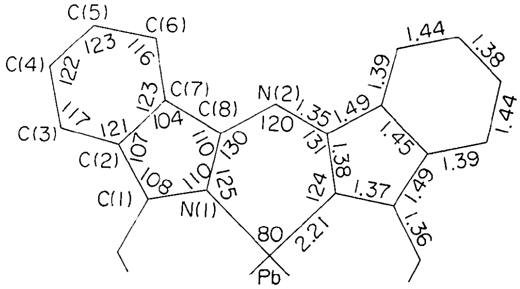


Fig. 3. Bond lengths (Å) and bond angles (°) for PbPc.

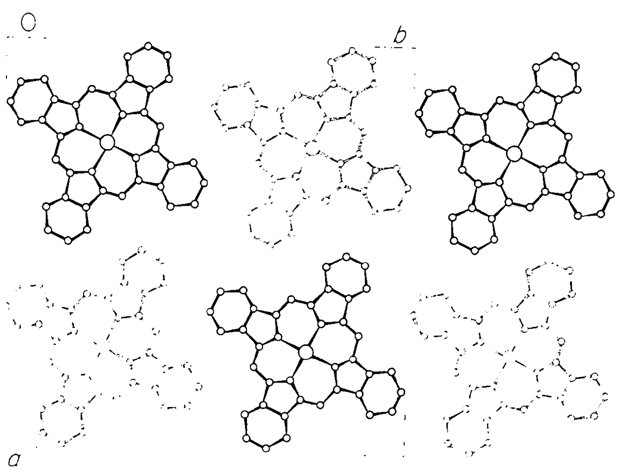


Fig. 4. The crystal structure viewed along the *c* axis.

Table 1. *Fractional coordinates of the atoms, their e.s.d.'s and isotropic temperature factors* (Å²)

	x	*y*	*z*	*B*
Pb	0·25	0·25	0·0	3·79
C(1)	0·133 (2)	0·261 (2)	0·294 (10)	3·0
C(2)	0·092 (1)	0·300 (1)	0·389 (12)	3·6
C(3)	0·039 (1)	0·295 (1)	0·469 (33)	3·9
C(4)	0·011 (1)	0·343 (1)	0·549 (22)	4·5
C(5)	0·036 (1)	0·391 (1)	0·549 (24)	4·5
C(6)	0·091 (1)	0·397 (1)	0·469 (34)	3·9
C(7)	0·117 (1)	0·351 (1)	0·389 (12)	3·6
C(8)	0·173 (2)	0·339 (2)	0·294 (10)	3·0
N(1)	0·180 (1)	0·287 (1)	0·243 (8)	3·2
N(2)	0·209 (1)	0·379 (1)	0·307 (7)	4·0
H(1)	0·019	0·258	0·469	7·0
H(2)	−0·031	0·341	0·614	7·0
H(3)	0·012	0·426	0·614	7·0
H(4)	0·111	0·436	0·469	7·0

Discussion. The temperature dependence of the electrical resistivity of PbPc films suggests that this substance is a one-dimensional conductor (Ukei, Takamoto & Kanda, to be published). The crystal structures of the phthalocyanines have been known since the determination by Robertson & Woodward (Robertson, 1936; Robertson & Woodward, 1937; Robertson & Woodward, 1940; Brown, 1968*a*, *b*; Friedel, Hoskins, Martin & Mason, 1970), but the crystal structure of PbPc has not yet been determined. The crystal structure analysis of PbPc was carried out in order to elucidate the one-dimensional character of this substance.

The observed bond distances and angles in PbPc are shown in Fig. 3. The best plane through the isoindole ring of a PbPc molecule makes an angle 76° with the fourfold axis of the molecule, and the lead atom deviates by 0·4 Å from the plane. The molecular structures of phthalocyanine complexes hitherto known are planar except for the case of SnPc (Friedel *et al.*, 1970). The non-planarity of the PbPc molecule may be explained by steric repulsion of the lead atom with the relatively large atomic radius and/or by such a square-pyramidal arrangement as is found in PbO (Moore & Pauling, 1941). The molecule stacks linearly parallel to the *c* axis (Fig. 1). The interatomic distance of lead atoms along the *c* axis (3·73 Å) is slightly larger than that of the pure metal (3·48 Å). This linear stacking structure of PbPc affords a basis for the one-dimensional conductor. While the reflexions with integral h' and k' are sharp, the reflexions with $h', k'=n+\frac{1}{2}$ are diffuse. As the diffuse reflexions are related to the sense of the molecule in this case, this regularity means that the range of order due to the sense of the molecule is rather short, although the lead atoms form a body-centered tetragonal lattice in the long range. This disorder is also consistent with the fact that the systematic absence $l=2n+1$ is partly violated in spite of the space group $P2_1/b$.

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Metavariscite – A Redetermination of its Crystal Structure

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Abstract. Metavariscite, $AlPO_4.2H_2O$, monoclinic, $P2_1/n$, $a=5·178$ (2), $b=9·514$ (2), $c=8·454$ (2) Å, $\beta=90·35$ (2)°, $Z=4$, $D_m=2·54$, $D_x=2·535$ g cm^{-3}. Material from Utalith Hill, Lucin, Utah, U.S.A.† PO_4 tetrahedra share vertices with four $AlO_4(OH_2)_2$ octahedra and *vice versa*. With Al···O distances of 1·892 (2) and 1·953 (2) Å the two waters coordinate the aluminum in *cis*-position and donate two single and quite short and two bifurcated longer hydrogen bonds, respectively, to phosphate oxygens. None of the hydrogen bonds is along an octahedron edge.

Introduction. Cell constants were determined from diffractometric measurements. The systematic absences are $h0l$ for $h+l$ odd and $0k0$ for k odd. The intensities of 1215 independent reflexions with $\theta \leq 30°$ were measured with Zr-filtered Mo $K\alpha$ radiation on a tape-controlled Siemens automatic diffractometer with $\theta/2\theta$ scan.

The crystal size was approximately 0·3 × 0·3 × 0·2 mm. 1067 reflexions had significant intensities. No correction for absorption ($\mu=8·2$ cm^{-1}) was applied. Least-squares refinement on F was started from non-hydrogen atom parameters reported by Borensztajn (1966). The four hydrogen atoms could easily be located as the highest peaks in a difference map. The final R was 0·027 for all reflexions (0·023 for significant reflexions only).

The form factors used were those of Hanson, Herman, Lea & Skillman (1964) for P, Al and O, and of Stewart, Davidson & Simpson (1965) for H. The observations were weighted according to $w=1/\sigma_F^2$ with σ_F evaluated from the measurements.

Table 1. *The atomic parameters and their standard deviations*

The B_{ij} in Å^2 are listed using the expression $\exp[-\frac{1}{4}(B_{11}h^2a^{*2}+2B_{23}klb^*c^*+\ldots)]$. Hydrogen atoms were refined anisotropically because a mixed-mode program was not available.

	x	y	z
Al	0·40309 (9)	0·32545 (5)	0·30626 (5)
P	−0·09105 (8)	0·14688 (4)	0·18371 (4)
O(1)	0·16505 (22)	0·17902 (11)	0·27036 (13)
O(2)	−0·09291 (23)	0·21677 (12)	0·02094 (13)
O(3)	−0·31481 (22)	0·20439 (12)	0·28127 (13)
O(4)	−0·11458 (21)	−0·01392 (11)	0·17227 (13)
O(*W*1)	0·11617 (30)	0·44767 (15)	0·32202 (18)
O(*W*2)	0·40410 (31)	0·36239 (14)	0·07903 (15)
H(11)	0·139 (5)	0·530 (3)	0·288 (4)
H(12)	−0·037 (7)	0·432 (3)	0·331 (5)
H(21)	0·274 (7)	0·334 (5)	0·023 (4)
H(22)	0·539 (8)	0·369 (5)	0·023 (4)

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† The sample (National Museum of Natural History catalog number 113753) was kindly provided by Mr John S. White Jr, Museum Specialist at the Smithsonian Institution, Division of Mineralogy, Washington D.C., U.S.A.