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Crystal and molecular structures of metal-free phthalocyanines, 1,2-dicyanobenzene tetramers* I. β form

Ryszard Kubiak and Jan Janczak
W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, PO Box 937, 50-950 Wrocław, Okólna 2 (Poland)

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Abstract

Phthalocyanine ($C_{32}H_{16}N_8$) is formed besides tin phthalocyanine in the reaction of $AuSn_4$ with 1,2-dicyanobenzene at 210 °C and crystallizes in the monoclinic system (space group, $P2_1/c$). The unit-cell parameters are $a=14.803(3)$ Å, $b=4.729(2)$ Å, $c=19.870(4)$ Å, $\beta=122.02(2)°$ and $Z=2$. The refined structure with anisotropic temperature factors for carbon and nitrogen atoms and isotropic for hydrogen atoms gave $R=0.0487$. The crystal structure data for metal-free phthalocyanines are discussed and compared with metal phthalocyanines. The phthalocyanine molecule is planar; the average derivation of the atoms from the phthalocyanine plane is 0.0257.

1. Introduction

Recently we published some results obtained from the X-ray analysis of the reaction products of 1,2-dicyanobenzene with Au–Cu and Au–Sn alloys [1]. This enabled us to undertake more systematic studies of the reaction of metals and alloys with 1,2-dicyanobenzene. In particular we are interested in recognizing the selective aspects of such reactions, *i.e.* (1) the possibility of definite metal separation from the appropriate alloy, and (2) the possibility of obtaining new phthalocyanines, also with more than one kind of metal in a definite compound.

In ref. 1 we gave information about the crystal structure of tin phthalocyanine (SnPc), formed as a main product of the reaction of tin or Au–Sn compounds with 1,2-dicyanobenzene. However, besides SnPc crystals, also a few other single crystals in the form of thin elongated plates were present in the reaction products. We took Weissenberg photographs of one of these crystals. These photographs indicated that it should be an H_2Pc crystal [2–4]. However, the formation of the H_2Pc form of 1,2-dicyanobenzene would have needed two additional hydrogen atoms for each four molecules of 1,2-dicyanobenzene in the reaction volume. However, in the literature it has been stated that phthalocyanine itself is rather unstable [5]. Therefore we decided to perform a crystal structure determination.

2. Experimental details

2.1. Preparation

Filings of $AuSn_4$ were mixed together with 1,2-dicyanobenzene in the mass proportions 1:1. The mixture was pressed into a pellet and heated in an evacuated and sealed glass tube at 210 °C for 1 week. Crystals of phthalocyanine (tetramer 1,2-dicyanobenzene) are formed besides SnPc [1].

2.2. Crystal data

The crystal data were as follows: $C_{32}H_{16}N_8$; $M_r=512$; monoclinic; $a=14.803(3)$ Å, $b=4.729(2)$ Å and $c=19.870(4)$ Å; $\beta=122.02(2)°$; $V=1179.3(2)$ Å^3; $Z=2$; $D_o=1.42$ g cm^{-3}; $D_c=1.443$ g cm^{-3}; $F(000)=528$; μ(Cu Kα) = 6.8 cm^{-1}; space group, $P2_1/c$; $T=298$ K.

A crystal of approximate dimensions $0.1\times0.15\times0.4$ mm was used for data collection on a four-circle Kuma diffraction KM-4 diffractometer with graphite-monochromated Cu Kα radiation. Preliminary examination by rotation and Weissenberg photographs indicated a space group of $P2_1/c$ which was used in the structure solution and refinement. Accurate lattice parameters were refined by the least-squares method fit of 20 reflections measured in the range $20°\leqslant2\vartheta\leqslant30°$.

*Dedicated to Professor Kazimierz Lukaszewicz on the occasion of his 65th birthday.

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4052 reflections were measured in the range $4° \leqslant 2\vartheta \leqslant 160°$ ($[(\sin\vartheta/\lambda)_{max} = 0.639$) using the ω–2ϑ scan technique with a scan speed of 0.025–0.1° s^{-1} and a scan width of 1.3°. The *hkl* range was as follows: *h*, $-15 \rightarrow 15$; *k*, $0 \rightarrow 5$; *l*, $-20 \rightarrow 20$. Two standard reflections ($22\bar{4}$ and 206) were monitored every 50 reflections. They showed no significant intensity variations. The measured intensities were corrected for Lorentz and polarization effects. No absorption correction was applied. 2143 unique reflections (1527 with $I > 2\sigma_I$; $R_{int} = 0.017$) were used in calculations.

2.3. Structure determination

The structure was solved by direct methods with the SHELXTL program system. All non-hydrogen atoms were located in the best *E* map and refined initially with isotropic and later with anisotropic thermal parameters. The difference map showed all hydrogen atoms. The inclusion of eight hydrogen atoms and refining by the full-matrix least-squares method with anisotropic thermal parameters for carbon and nitrogen atoms and isotropic for hydrogen atoms gave $R = 0.0487$. The function minimized was $\Sigma\omega(|F_o| - |F_o|)^2$ with $\omega = 1/\sigma_F^2$.

TABLE 1. Final atomic coordinates and equivalent isotropic thermal parameters with estimated standard deviations in parentheses; $U_{eq} = 1/3\Sigma_i\Sigma_j a_i a_j a_i^* a_j^*$

Atom	*x*	*y*	*z*	U_{eq}
N(1)	0.25479(22)	0.02721(62)	0.16180(17)	0.0308(13)
N(2)	0.07563(21)	0.21763(62)	0.09926(16)	0.0298(13)
N(3)	−0.07335(21)	0.50012(65)	0.07943(16)	0.0310(13)
N(4)	−0.13461(21)	0.19246(61)	−0.03466(16)	0.0298(13)
C(1)	0.18122(26)	0.19553(75)	0.15956(19)	0.0292(15)
C(2)	0.20140(26)	0.39153(75)	0.22256(20)	0.0300(15)
C(3)	0.29194(29)	0.45179(86)	0.29572(22)	0.0373(17)
C(4)	0.28230(31)	0.65148(95)	0.34277(23)	0.0424(18)
C(5)	0.18573(32)	0.78962(92)	0.31797(23)	0.0423(19)
C(6)	0.09561(30)	0.73035(84)	0.24456(22)	0.0371(18)
C(7)	0.10502(26)	0.52822(76)	0.19759(20)	0.0295(15)
C(8)	0.02714(26)	0.41690(73)	0.11984(20)	0.0297(15)
C(9)	−0.14646(26)	0.39608(74)	0.00929(20)	0.0294(15)
C(10)	−0.25702(26)	0.48845(78)	−0.03233(20)	0.0306(15)
C(11)	−0.30934(30)	0.68568(85)	−0.01288(23)	0.0378(18)
C(12)	−0.41740(31)	0.72279(93)	−0.06636(24)	0.0442(20)
C(13)	−0.47173(30)	0.56930(89)	−0.13716(25)	0.0436(19)
C(14)	−0.41934(29)	0.37219(88)	−0.15659(23)	0.0384(17)
C(15)	−0.31108(26)	0.33443(74)	−0.10312(20)	0.0307(16)
C(16)	−0.23199(26)	0.15033(76)	−0.10295(20)	0.0295(15)
H(1)	0.3609(30)	0.3700(88)	0.3139(21)	0.046(11)
H(2)	0.3441(30)	0.6953(90)	0.3961(22)	0.047(11)
H(3)	0.1812(30)	0.9114(91)	0.3559(23)	0.051(12)
H(4)	0.0272(30)	0.8270(90)	0.2300(22)	0.048(11)
H(5)	−0.2730(30)	0.8005(93)	0.0380(23)	0.052(12)
H(6)	−0.4573(32)	0.8367(100)	−0.0534(24)	0.058(13)
H(7)	−0.5522(30)	0.6070(87)	−0.1732(22)	0.049(11)
H(8)	−0.4572(29)	0.2705(90)	−0.2098(22)	0.050(12)

TABLE 2. Bond lengths and angles with estimated standard deviations in parentheses

Bond length (Å)			
N(1)–C(1)	1.330(5)	C(3)–H(1)	0.965(43)
N(2)–C(1)	1.380(4)	C(4)–H(2)	0.987(30)
C(1)(–C(2)	1.456(5)	C(5)–H(3)	0.979(49)
C(2)–C(3)	1.387(4)	C(6)–H(4)	1.004(44)
C(3)–C(4)	1.388(7)	C(11)–H(5)	1.015(40)
C(4)–C(5)	1.402(6)	C(12)–H(6)	0.932(54)
C(5)–C(6)	1.386(5)	C(13)–H(7)	1.029(37)
C(6)–C(7)	1.393(6)	C(14)–H(8)	1.017(39)
C(7)–C(8)	1.451(4)		
C(8)–N(2)	1.372(5)		
C(8)–N(3)	1.321(4)		
N(3)–C(9)	1.325(4)		
C(9)–N(4)	1.372(5)		
C(9)–C(10)	1.455(5)		
C(10)–C(11)	1.392(7)		
C(11)–C(12)	1.384(5)		
C(12)–C(13)	1.397(6)		
C(13)–C(14)	1.392(7)		
C(14)–C(15)	1.387(4)		
C(15)–C(10)	1.398(5)		
C(15)–C(16)	1.458(6)		
C(16)–N(4)	1.373(3)		
$C(16)^i$–N(1)	1.330(5)		
Angles (deg)			
$C(16)^i$–N(1)–C(1)	121.8(3)	C(2)–C(3)–H(1)	123.5(3)
N(1)–C(1)–N(2)	127.2(3)	H(1)–C(3)–C(4)	119.1(2)
N(1)–C(1)–C(2)	124.1(3)	C(3)–C(4)–H(2)	119.9(3)
N(2)–C(1)–C(2)	108.7(3)	H(2)–C(4)–C(5)	118.1(3)
C(1)–C(2)–C(7)	106.5(3)	C(4)–C(5)–H(3)	118.5(2)
C(1)–C(2)–C(3)	132.5(4)	H(3)–C(5)–C(6)	120.6(2)
C(7)–C(2)–C(3)	121.0(4)	C(5)–C(6)–H(4)	118.2(2)
C(2)–C(3)–C(4)	117.3(4)	H(4)–C(6)–C(7)	124.2(2)
C(3)–C(4)–C(5)	122.0(3)	C(10)–C(11)–H(5)	123.8(3)
C(4)–C(5)–C(6)	120.6(4)	H(5)–C(11)–C(12)	118.9(3)
C(5)–C(6)–C(7)	117.5(4)	C(11)–C(12)–H(6)	120.3(2)
C(6)–C(7)–C(2)	121.7(3)	H(6)–C(12)–C(13)	117.9(2)
C(6)–C(7)–C(8)	131.1(3)	C(12)–C(13)–H(7)	116.6(3)
C(2)–C(7)–C(8)	107.2(3)	H(7)–C(13)–C(14)	122.1(3)
C(7)–C(8)–N(2)	108.7(3)	C(13)–C(14)–H(8)	121.6(3)
N(2)–C(8)–N(3)	128.5(3)	H(8)–C(14)–C(15)	120.8(3)
C(8)–N(3)–C(9)	123.8(4)		
N(3)–C(9)–N(4)	128.4(3)		
N(3)–C(9)–C(10)	122.1(4)		
N(4)–C(9)–C(10)	109.5(3)		
C(9)–C(10)–C(15)	106.7(4)		
C(9)–C(10)–C(11)	131.8(3)		
C(10)–C(11)–C(12)	117.3(4)		
C(11)–C(12)–C(13)	121.4(5)		
C(12)–C(13)–C(14)	121.3(3)		
C(13)–C(14)–C(15)	117.5(3)		
C(14)–C(15)–C(10)	121.1(4)		
C(14)–C(15)–C(16)	132.8(3)		
C(10)–C(15)–C(16)	106.2(3)		
C(15)–C(16)–N(4)	109.7(3)		

Symmetry code *i*, $-x$, $-y$, $-z$.

The final values were $R = 0.0487$, $\omega R = 0.0548$ and $S = 1.02$ for 213 refined parameters ($R = 0.0778$ and $\omega R = 0.0738$ for all 2143 reflections). The residual elec-

tron density in the final difference Fourier synthesis was -0.28–0.29 electron Å^{-3}; $\Delta/\sigma=0.01$. The atomic scattering factors were supplied by the SHELXTL program. All calculations were performed on an IBM PC/AT. The final atomic parameters are given in Table 1, and the bond lengths and angles in Table 2.

3. Description of the structure and discussion

The molecular geometry and numbering of the atoms used in this paper are given in Fig. 1. There are two centrosymmetrical molecules in the unit cell. A view of stereopacking of unit cell content is shown in Fig. 2.

The phthalocyanine molecule is planar. The equation of the mean plane through the tetramer, referred to standard orthogonal axes, is $0.2227X+0.7160Y-0.6616Z=0$. The mean displacement of the carbon, nitrogen and hydrogen atoms from this plane is 0.0257, randomly above and below. The normal to the mean plane of the phthalocyanine ring makes an angle of 44.3° with the *b* axis. The perpendicular distance between successive planes of phthalocyanine molecules along *b* is 3.318 Å. Figure 3 shows the mutual arrangement of phthalocyanine molecules. The angle between the two planes of molecules is 88.5°.

The peripheral benzene rings are not perfectly hexagonal, an effect noted previously in metallophthalocyanines [6–9] and also in H_2Pc [3]. The mean C–N bond length in the central 16-membered ring is 1.350 Å which is exactly that required for a bond order of 1.5. However, the C–N bonds attached to *N*-isoindole rings (mean C–N length of 1.374 Å) are evidently longer than those attached to nitrogen between isoindole rings (mean C–N length, 1.326 Å). This could be due to the influence of the π-electron-resonating system in isoindole rings, and the C–C bonds in these rings with a mean length of 1.455 Å have a bond order of 1.25.

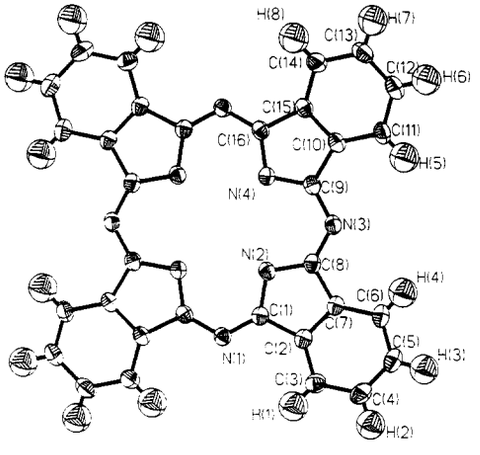

Fig. 1. A view of the molecule with the atomic numbering scheme.

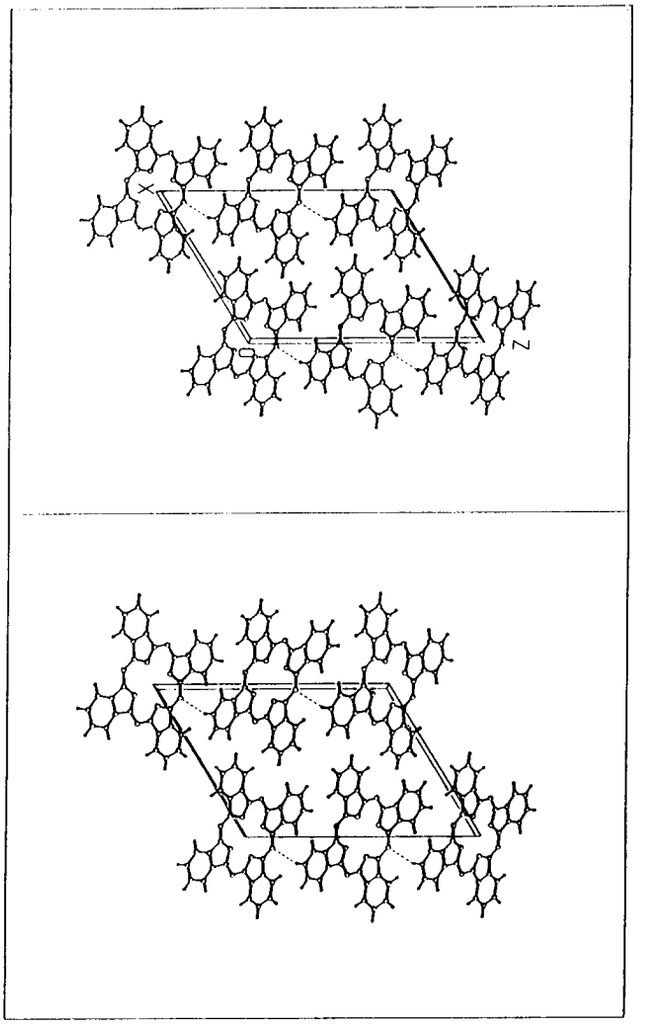

Fig. 2. Stereopacking of the phthalocyanine molecules in a unit cell.

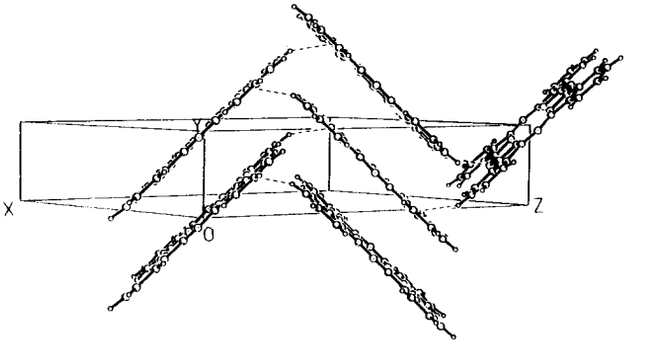

Fig. 3. The arrangement of the molecules in the unit cell.

Although the results proved that the measured crystal was a 1,2-dicyanobenzene tetramer (phthalocyanine), we checked our results also for H_2Pc structure models [3, 4]. However, the supplementary hydrogen atoms

introduced into appropriate central positions of the phthalocyanine molecule ring were consequently rejected during refining cycles.

An interesting observation was that the (100) planes of the phthalocyanine crystal are cleavage planes, *e.g.* the interaction between the phthalocyanine molecules in the [001] and [010] directions is greater than in the [100] direction. This is consistent with the existence and geometry of very weak hydrogen bonding (see Figs. 2 and 3); N(3)–H(3)^{i} the distance is 2.559 Å (where I$\equiv -x, 0.5+y, 0.5-z$).

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References

1 J. Janczak and R. Kubiak, *J. Alloys Comp., 190* (1992) 121.
2 J. M. Robertson, *J. Chem. Soc.,* (1936) 1195–1209.
3 B. F. Hoskins and S. A. Mason, *Chem. Commun.,* (1969), 544–555.
4 H. Höchst, A. Goldman, S. Hüfner and H. Malter, *Phys. Status Solidi B, 76* (1976) 559–568.
5 B. D. Berezin, *Koordinacionnye Soedinenija Porfirinow i Ftalocianina,* Moscow, 1978, pp. 32–42 (in Russian).
6 G. A. Williams, B. N. Figgis, R. Mason, S. A. Mason and P. E. Fielding, *J. Chem. Soc., Dalton Trans.,* (1980) 1688–1692.
7 C. J. Brown, *J. Chem. Soc. A,* (1968) 2494–2498.
8 B. N. Figgis, E. S. Kucharski and G. A. Williams, *J. Chem. Soc., Dalton Trans.,* (1980) 1515–1525.
9 C. J. Brown, *J. Chem. Soc. A,* (1968) 2488–2493.