

# X-ray analysis of phthalocyanines formed in the reaction of Au–Cu and Au–Sn alloys with 1,2-dicyanobenzene\*

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## Abstract

X-ray investigations of the reactions of copper, tin and their alloys with gold, with 1,2-dicyanobenzene at 210 °C have been performed. It was found that under the conditions used, gold does not take part in the reaction with 1,2-dicyanobenzene, but separates from the alloys. Copper and tin phthalocyanines are formed as the main products of the above reactions. The crystal structure of tin phthalocyanine (SnPC) has been determined. SnPC crystallizes in the triclinic system ( $a = 12.048(3)$  Å,  $b = 12.630(3)$  Å,  $c = 8.671(3)$  Å,  $\alpha = 95.85(5)^\circ$ ,  $\beta = 95.10(5)^\circ$ ,  $\gamma = 68.25(5)^\circ$ ), space group  $P\bar{1}$ ,  $Z = 2$ . The refined structure with anisotropic temperature factors gave  $R = 0.041$ . The Sn atom is coordinated by four isoindole N atoms, the average Sn–N distance being 2.267(6) Å. The SnPc molecule is not planar. The Sn atom is 1.1286 Å out of the plane of the four coordinating N atoms.

## 1. Introduction

In previous papers we studied the oxidation susceptibility of copper and copper alloyed with gold [1, 2]. We found that at a temperature somewhere above 200 °C Cu–Au compounds oxidize in air as easily as pure copper. Recently we proved that filings of tin as well AuSn<sub>4</sub>, AuSn<sub>2</sub> and AuSn annealed at 210 °C in air are practically unaffected by oxygen even after months of exposure. The atomic radius of copper (1.35 Å) is much smaller than that of tin (1.45 Å). Therefore one can assume that the mobility of Sn atoms in the overall crystalline matrix of particular Au–Sn compounds is much smaller than the mobility of Cu atoms in their corresponding gold compounds. We were interested to find out if this can play an essential role in the chemical stability of Au–Sn compounds. Therefore we decided to examine how Au–Cu and Au–Sn alloys react with other media. Here we present the results of the reaction with 1,2-dicyanobenzene.

## 2. Experimental details

### 2.1. Preparation

Filings of each metallic sample (copper, AuCu<sub>3</sub>, Au<sub>3</sub>Cu, tin, AuSn<sub>4</sub>, AuSn) were mixed with 1,2-dicy-

anobenzene in the weight ratio 1:1. Each mixture was pressed into a pellet and heated in an evacuated and sealed glass tube at 210 °C for 1 week. The products showed well-shaped crystals. We found that the reaction proceeded equally well for pure copper or tin as for their gold alloys. However, when the compounds were used as substrates, the single crystals in the products were bigger.

### 2.2. X-ray analysis

#### 2.2.1. Powder samples

The measurements were performed on a Stoe powder diffractometer equipped with a position-sensitive detector [3, 4] using monochromatized Cu K $\alpha_1$  radiation. Analysis of diagrams of the samples obtained from the reaction of copper and Au–Cu compounds with 1,2-dicyanobenzene showed that in the products  $\beta$ -Cu phthalocyanine was formed (CuPc) [5]. The powder diffraction diagram obtained from the reaction of the compound richest in gold (Au<sub>3</sub>Cu) with 1,2-dicyanobenzene showed additionally distinct lines from crystalline gold.

The X-ray diagrams of the reaction products of tin and Au–Sn compounds with 1,2-dicyanobenzene showed a different, more complicated structure. The angular position of the strongest diffraction lines observed indicated that in these cases triclinic SnPc was probably formed [6]. However, since the atomic positions of triclinic SnPc have not been published and because orthorhombic SnPc<sub>2</sub> is also known [7], we were unable

\*Dedicated to Professor Erich Wölfel on the occasion of his 70th birthday.

TABLE 1. Final atomic coordinates and equivalent isotropic thermal parameters  $U_{eq}$ , with estimated standard deviations in parentheses ( $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i a_j^* a_j^*$ )

| Atom  | x          | y          | z          | $U_{eq}$   |
|-------|------------|------------|------------|------------|
| Sn    | 0.2479(1)  | 0.0062(1)  | 0.2015(1)  | 0.0306(2)  |
| N(1)  | 0.3561(5)  | -0.2973(5) | 0.2341(7)  | 0.0337(20) |
| N(2)  | 0.4243(5)  | -0.1368(5) | 0.2573(7)  | 0.0320(20) |
| N(3)  | 0.5522(5)  | -0.0283(5) | 0.3248(7)  | 0.0314(20) |
| N(4)  | 0.3912(5)  | 0.0696(5)  | 0.1421(7)  | 0.0300(20) |
| N(5)  | 0.2726(6)  | 0.2110(5)  | -0.0353(7) | 0.0319(21) |
| N(6)  | 0.1981(5)  | 0.0567(5)  | -0.0451(7) | 0.0317(21) |
| N(7)  | 0.0834(5)  | -0.0631(4) | -0.1398(7) | 0.0268(20) |
| N(8)  | 0.2268(5)  | -0.1502(5) | 0.0704(7)  | 0.0288(21) |
| C(1)  | 0.4288(6)  | -0.2444(6) | 0.2843(8)  | 0.0303(22) |
| C(2)  | 0.5397(7)  | -0.2992(6) | 0.3819(8)  | 0.0320(24) |
| C(3)  | 0.5843(7)  | -0.4044(6) | 0.4371(9)  | 0.0445(30) |
| C(4)  | 0.6894(7)  | -0.4296(7) | 0.5328(9)  | 0.0468(31) |
| C(5)  | 0.7430(7)  | -0.3493(8) | 0.5618(9)  | 0.0588(35) |
| C(6)  | 0.6993(6)  | -0.2462(7) | 0.5008(9)  | 0.0436(31) |
| C(7)  | 0.5941(6)  | -0.2208(6) | 0.4087(8)  | 0.0302(25) |
| C(8)  | 0.5202(7)  | -0.1179(6) | 0.3277(8)  | 0.0313(27) |
| C(9)  | 0.4929(7)  | 0.0556(7)  | 0.2354(9)  | 0.0347(29) |
| C(10) | 0.5317(6)  | 0.1521(6)  | 0.2213(9)  | 0.0326(26) |
| C(11) | 0.6230(6)  | 0.1819(6)  | 0.2940(9)  | 0.0384(27) |
| C(12) | 0.6313(7)  | 0.2842(8)  | 0.2554(9)  | 0.0481(33) |
| C(13) | 0.5538(7)  | 0.3489(7)  | 0.1484(9)  | 0.0442(30) |
| C(14) | 0.4624(6)  | 0.3183(6)  | 0.0731(6)  | 0.0394(28) |
| C(15) | 0.4509(7)  | 0.2211(6)  | 0.1134(8)  | 0.0314(27) |
| C(16) | 0.3640(6)  | 0.1661(6)  | 0.0679(9)  | 0.0318(27) |
| C(17) | 0.1987(7)  | 0.1576(6)  | -0.0903(9) | 0.0312(27) |
| C(18) | 0.1090(7)  | 0.1973(7)  | -0.2155(8) | 0.0318(27) |
| C(19) | 0.0755(7)  | 0.2934(6)  | -0.3005(8) | 0.0403(29) |
| C(20) | -0.0138(8) | 0.3048(7)  | -0.4157(9) | 0.0464(31) |
| C(21) | -0.0659(7) | 0.2228(7)  | -0.4508(9) | 0.0455(31) |
| C(22) | -0.0317(6) | 0.1264(6)  | -0.3682(9) | 0.0375(27) |
| C(23) | 0.0563(6)  | 0.1153(6)  | -0.2482(8) | 0.0285(26) |
| C(24) | 0.1123(7)  | 0.0256(7)  | -0.1398(8) | 0.0320(28) |
| C(25) | 0.1385(6)  | -0.1471(6) | -0.0453(9) | 0.0280(26) |
| C(26) | 0.1184(6)  | -0.2526(6) | -0.0592(8) | 0.0271(25) |
| C(27) | 0.0449(6)  | -0.2958(6) | -0.1555(8) | 0.0340(26) |
| C(28) | 0.0510(7)  | -0.4042(6) | -0.1410(9) | 0.0417(30) |
| C(29) | 0.1310(7)  | -0.4732(7) | -0.0285(9) | 0.0443(31) |
| C(30) | 0.2032(6)  | -0.4316(6) | 0.0669(8)  | 0.0346(26) |
| C(31) | 0.1973(6)  | -0.3206(7) | 0.0554(8)  | 0.0281(25) |
| C(32) | 0.2640(7)  | -0.2533(7) | 0.1280(9)  | 0.0325(29) |
| H(1)  | 0.5461     | -0.4589    | 0.4120     | 0.07       |
| H(2)  | 0.7238     | -0.5015    | 0.5786     | 0.07       |
| H(3)  | 0.8153     | -0.3673    | 0.6283     | 0.07       |
| H(4)  | 0.7398     | -0.1933    | 0.5199     | 0.07       |
| H(5)  | 0.6784     | 0.1351     | 0.3684     | 0.07       |
| H(6)  | 0.6934     | 0.3083     | 0.3053     | 0.07       |
| H(7)  | 0.5621     | 0.4180     | 0.1243     | 0.07       |
| H(8)  | 0.4090     | 0.3638     | -0.0044    | 0.07       |
| H(9)  | 0.1129     | 0.3499     | -0.2796    | 0.07       |
| H(10) | -0.0410    | 0.3712     | -0.4741    | 0.07       |
| H(11) | -0.1271    | 0.2337     | -0.5335    | 0.07       |
| H(12) | -0.0670    | 0.0694     | -0.3927    | 0.07       |
| H(13) | -0.0098    | -0.2499    | -0.2318    | 0.07       |
| H(14) | 0.0006     | -0.4348    | -0.2079    | 0.07       |
| H(15) | 0.1339     | -0.5494    | -0.0199    | 0.07       |
| H(16) | 0.2585     | -0.4787    | 0.1420     | 0.07       |

TABLE 2. Bond lengths (Å) and angles (deg), with estimated standard deviations in parentheses

|                   |           |                   |           |
|-------------------|-----------|-------------------|-----------|
| Sn-N(2)           | 2.273(5)  | C(16)-N(5)        | 1.324(11) |
| Sn-N(4)           | 2.271(8)  | N(5)-C(17)        | 1.333(12) |
| Sn-N(6)           | 2.260(7)  | C(17)-N(6)        | 1.374(11) |
| Sn-N(8)           | 2.263(7)  | C(17)-C(18)       | 1.449(10) |
| N(1)-C(1)         | 1.307(10) | C(18)-C(19)       | 1.403(12) |
| C(1)-N(2)         | 1.382(11) | C(19)-C(20)       | 1.379(11) |
| C(1)-C(2)         | 1.487(10) | C(20)-C(21)       | 1.394(15) |
| C(2)-C(3)         | 1.355(8)  | C(21)-C(22)       | 1.385(12) |
| C(2)-C(7)         | 1.368(11) | C(22)-C(23)       | 1.397(11) |
| C(3)-C(4)         | 1.401(10) | C(23)-C(18)       | 1.397(13) |
| C(4)-C(5)         | 1.383(13) | C(23)-C(24)       | 1.445(10) |
| C(5)-C(6)         | 1.355(13) | C(24)-N(6)        | 1.389(11) |
| C(6)-C(7)         | 1.381(8)  | C(23)-N(7)        | 1.328(12) |
| C(7)-C(8)         | 1.485(10) | N(7)-C(25)        | 1.340(10) |
| C(8)-N(2)         | 1.346(11) | C(25)-N(8)        | 1.388(10) |
| C(8)-N(3)         | 1.327(12) | C(25)-C(26)       | 1.431(12) |
| N(3)-C(9)         | 1.320(10) | C(26)-C(27)       | 1.384(12) |
| C(9)-N(4)         | 1.371(10) | C(27)-C(28)       | 1.361(12) |
| C(9)-C(10)        | 1.477(12) | C(28)-C(29)       | 1.423(11) |
| C(10)-C(11)       | 1.371(9)  | C(29)-C(30)       | 1.356(12) |
| C(11)-C(12)       | 1.409(13) | C(30)-C(31)       | 1.390(11) |
| C(12)-C(13)       | 1.355(11) | C(31)-C(26)       | 1.424(10) |
| C(13)-C(14)       | 1.387(13) | C(31)-C(32)       | 1.439(11) |
| C(14)-C(15)       | 1.368(9)  | C(32)-N(8)        | 1.344(10) |
| C(15)-C(10)       | 1.400(10) | C(32)-N(1)        | 1.361(10) |
| C(15)-C(16)       | 1.464(13) |                   |           |
| C(16)-N(4)        | 1.354(10) |                   |           |
| N(2)-Sn-N(4)      | 75.0(2)   | C(16)-N(4)-Sn     | 121.9(5)  |
| N(2)-Sn-N(6)      | 119.8(2)  | N(4)-C(16)-N(5)   | 128.1(8)  |
| N(2)-Sn-N(8)      | 76.5(2)   | C(16)-N(5)-C(17)  | 122.5(7)  |
| N(4)-Sn-N(6)      | 75.2(2)   | N(5)-C(17)-N(6)   | 126.8(7)  |
| N(4)-Sn-N(8)      | 120.7(2)  | C(17)-N(6)-Sn     | 122.1(5)  |
| N(1)-C(1)-N(2)    | 130.0(6)  | N(6)-C(17)-C(18)  | 109.7(7)  |
| N(1)-C(1)-C(2)    | 122.3(7)  | C(17)-N(6)-C(24)  | 107.4(7)  |
| N(2)-C(1)-C(2)    | 107.7(7)  | C(17)-C(18)-C(23) | 106.7(7)  |
| C(1)-C(2)-C(7)    | 106.3(7)  | C(19)-C(18)-C(23) | 121.8(9)  |
| C(3)-C(2)-C(7)    | 123.6(6)  | C(18)-C(19)-C(20) | 116.4(8)  |
| C(2)-C(3)-C(4)    | 116.5(4)  | C(19)-C(20)-C(21) | 122.5(8)  |
| C(3)-C(4)-C(5)    | 119.3(8)  | C(20)-C(21)-C(22) | 121.1(7)  |
| C(4)-C(5)-C(6)    | 123.2(8)  | C(21)-C(22)-C(23) | 117.3(7)  |
| C(5)-C(6)-C(7)    | 117.2(8)  | C(22)-C(23)-C(18) | 121.0(4)  |
| C(6)-C(7)-C(2)    | 119.9(6)  | C(18)-C(23)-C(24) | 106.6(7)  |
| C(2)-C(7)-C(8)    | 107.8(7)  | C(23)-C(24)-N(6)  | 109.5(8)  |
| C(7)-C(8)-N(2)    | 107.9(8)  | C(24)-N(6)-Sn     | 123.2(6)  |
| C(8)-N(2)-C(1)    | 110.3(6)  | N(6)-C(24)-N(7)   | 128.2(8)  |
| C(1)-N(2)-Sn      | 121.4(5)  | C(24)-N(7)-C(25)  | 123.1(7)  |
| C(8)-N(2)-Sn      | 123.0(5)  | N(7)-C(25)-N(8)   | 126.9(8)  |
| N(2)-C(8)-N(3)    | 129.3(7)  | C(25)-N(8)-Sn     | 124.6(4)  |
| C(8)-N(3)-C(9)    | 121.4(7)  | N(8)-C(25)-C(26)  | 110.0(6)  |
| N(3)-C(9)-N(4)    | 128.6(9)  | C(25)-C(26)-C(31) | 105.9(6)  |
| C(9)-N(4)-Sn      | 122.3(6)  | C(31)-C(26)-C(27) | 120.0(6)  |
| N(4)-C(9)-C(10)   | 108.9(7)  | C(26)-C(27)-C(28) | 119.1(6)  |
| C(9)-C(10)-C(15)  | 106.5(7)  | C(27)-C(28)-C(29) | 121.2(8)  |
| C(15)-C(10)-C(11) | 120.9(8)  | C(28)-C(29)-C(30) | 120.1(8)  |
| C(10)-C(11)-C(12) | 117.2(6)  | C(29)-C(30)-C(31) | 119.6(6)  |
| C(11)-C(12)-C(13) | 121.1(9)  | C(30)-C(31)-C(26) | 120.0(3)  |
| C(12)-C(13)-C(14) | 121.8(9)  | C(26)-C(30)-C(32) | 105.6(5)  |
| C(13)-C(14)-C(15) | 117.6(6)  | C(31)-C(32)-N(8)  | 111.2(6)  |
| C(14)-C(15)-C(10) | 121.2(3)  | C(32)-N(8)-C(25)  | 107.3(7)  |
| C(10)-C(15)-C(16) | 105.4(7)  | C(32)-N(8)-Sn     | 123.8(5)  |
| C(15)-C(16)-N(4)  | 110.8(6)  | N(8)-C(32)-N(1)   | 127.6(8)  |
| C(16)-N(4)-C(9)   | 108.3(7)  | C(32)-N(1)-C(1)   | 122.0(7)  |

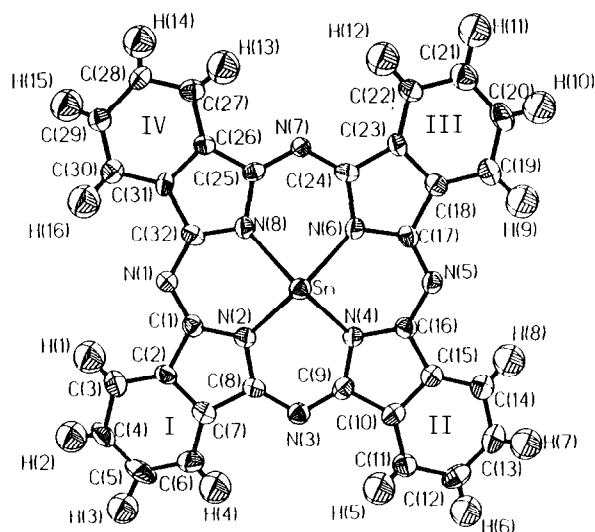


Fig. 1. View of SnPc molecule with atomic numbering scheme.

to compare precisely the obtained X-ray diagrams with theoretical ones. This led us to perform a structure determination on a selected crystal.

### 2.2.2. Single crystal

Crystal data: tin phthalocyanine,  $\text{SnC}_{32}\text{H}_8\text{N}_4$ ,  $M_r = 631.2$ , triclinic,  $a = 12.048(3) \text{ \AA}$ ,  $b = 12.630(3) \text{ \AA}$ ,  $c = 8.671(3) \text{ \AA}$ ,  $\alpha = 95.85(5)^\circ$ ,  $\beta = 95.10(5)^\circ$ ,  $\gamma = 68.25(5)^\circ$ ,  $V = 1217.2(3) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_o = 1.71 \text{ g cm}^{-3}$ ,  $D_c = 1.722 \text{ g cm}^{-3}$ ,  $F(000) = 628$ ,  $\mu(\text{Mo K}\alpha) = 10.9 \text{ cm}^{-1}$ , space group  $P\bar{1}$ .

A crystal of approximate dimensions  $0.16 \times 0.20 \times 0.25$  mm chosen from the reaction product of  $\text{AuSn}_4$  with 1,2-dicyanobenzene was used for data collection on a

four-circle Kuma Diffraction KM-4 diffractometer with graphite-monochromatized Mo  $\text{K}\alpha$  radiation. Initially the unit cell parameters were determined from single-crystal oscillations and Weissenberg photographs. Accurate lattice parameters were refined by the least-squares fitting of 20 reflections measured in the range  $15^\circ \leq 2\theta \leq 25^\circ$ . A total of 6233 reflections were measured in the range  $3 \leq 2\theta \leq 50^\circ$  ( $(\sin \theta/\lambda)_{\text{max}} = 0.5947$ ) using the  $\omega/2\theta$  scan technique with a scan speed of  $0.08 \text{ deg s}^{-1}$  and a scan width of  $1.5^\circ$ . The  $hkl$  range was  $h: -12 \rightarrow 12$ ,  $k: -13 \rightarrow 13$ ,  $l: -9 \rightarrow 9$ . Two standard reflections ( $(\bar{1}02)$ ,  $(012)$ ) were monitored every 50 reflections. They showed no significant intensity variations. The measured intensities were corrected for Lorentz and polarization effects. No absorption corrections were made ( $\mu = 10.9 \text{ cm}^{-1}$ ).

### 2.3. Structure determination

A total of 3443 independent reflections (2775 with  $I > 2\sigma_I$ ,  $R_{\text{int}} = 0.028$ ) were used in subsequent calculations. The heavy atom (Sn) position was obtained from the three-dimensional Patterson map. The remaining non-hydrogen atoms were located by different Fourier calculations. The structure was refined by the block matrix least-squares method with anisotropic temperature factors (using the SHELXTL programme system, 1991), which gave an  $R$  factor of 0.0464 and  $R_w = 0.0664$ . Inclusion of 16 H atoms in their calculated positions and a few more cycles of block matrix least-squares refinement reduced  $R$  to 0.0415 and  $R_w$  to 0.0634. The H atom position location with the geometrical correlation, the isotropic temperature factor for all H atoms was fixed,  $U_{\text{iso}} = 0.07$ . The function minimized was

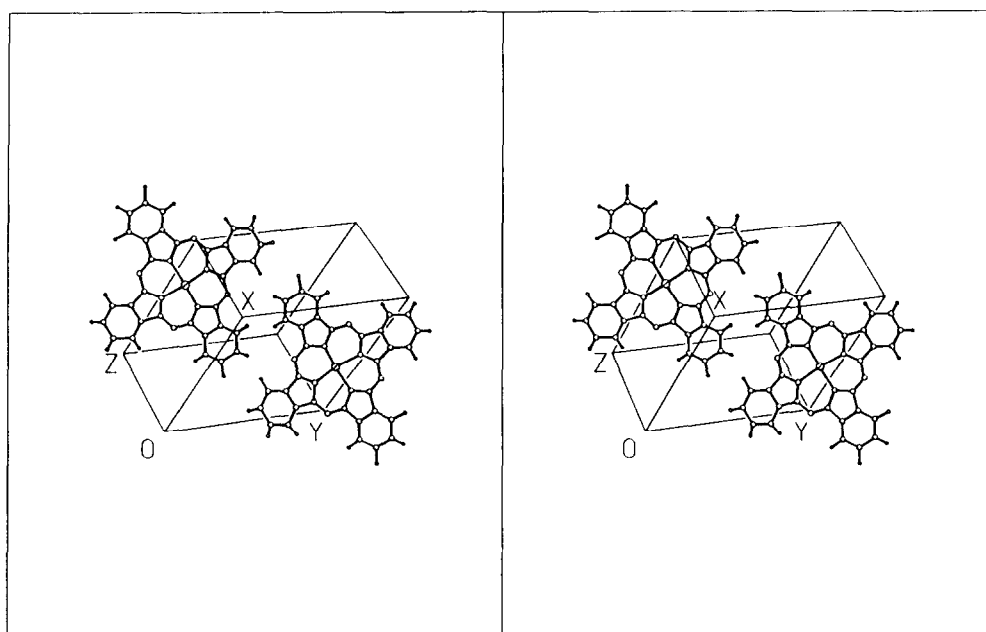


Fig. 2. View of stereopacking of unit cell content.

TABLE 3. Least-squares plane data

| Plane | Atoms defining plane  | $l$     | $m$     | $n$     | $p$     |
|-------|---|---------|---------|---------|---------|
| (a)   | Least-squares planes and their equations given by $lX+mY+nZ-p=0$ , where $X$ , $Y$ and $Z$ are orthogonal coordinates ( $\text{\AA}$ ), $l$ , $m$ and $n$ are the direction cosines of the normal to the plane and $p$ is the distance of the plane from the origin |         |         |         |         |
| 1     | N(2), N(4), N(6), N(8)  | -0.6076 | 0.2861  | 0.7410  | -1.3862 |
| 2     | C(2)-C(7)   | -0.5330 | 0.2014  | 0.8218  | -0.9437 |
| 3     | C(10)-C(15)   | -0.6011 | 0.3191  | 0.7327  | -1.3682 |
| 4     | C(18)-C(23)   | 0.6999  | -0.2580 | -0.6660 | 1.5825  |
| 5     | C(26)-C(31)   | -0.7104 | -0.0979 | -0.6970 | 1.4107  |
| (b)   | Deviations ( $\text{\AA}$ ) of relevant atoms from least-squares planes defined above   |         |         |         |         |
| 1     | N(2), -0.0072; N(4), 0.0073; N(6), -0.0073; N(8), 0.0071  |         |         |         |         |
| 2     | C(2), 0.0121; C(3), -0.0149; C(4), 0.0041; C(5), 0.0094; C(6), -0.0125; C(7), 0.0017  |         |         |         |         |
| 3     | C(10), -0.0040; C(11), -0.0083; C(12), 0.0097; C(13), 0.0013; C(14), -0.0138; C(15), 0.0152   |         |         |         |         |
| 4     | C(18), -0.0016; C(19), 0.0106; C(20), -0.0106; C(21), 0.0014; C(22), 0.0077; C(23), -0.0075   |         |         |         |         |
| 5     | C(26), 0.0083; C(27), -0.0017; C(28), -0.0027; C(29), 0.0004; C(30), 0.0063; C(31), -0.0105   |         |         |         |         |

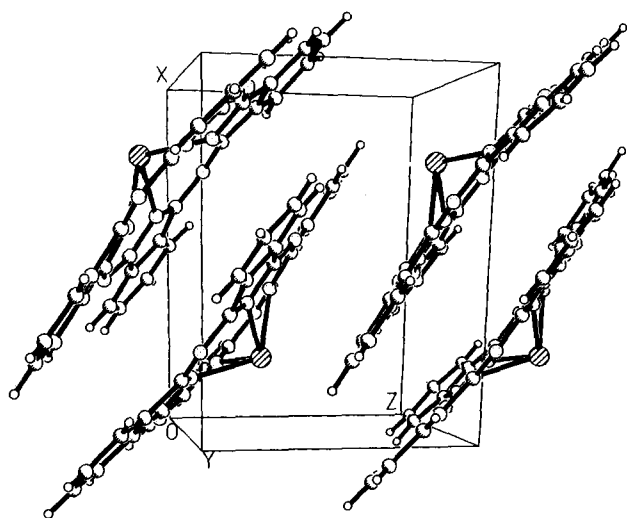


Fig. 3. Arrangement of molecules in unit cell.

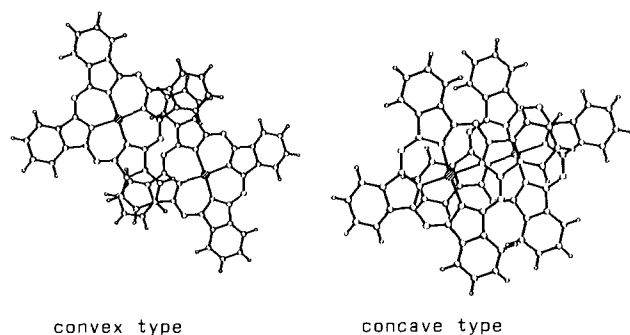


Fig. 4. Overlap of neighbouring molecules in convex- and concave-type pairs.

$\sum w(|F_o| - |F_c|)^2$  with the weighting scheme  $w = [\sigma^2(F_o) + (0.00417 F_o)^2]^{-1}$ . The final values obtained were  $R = 0.0405$ ,  $R_w = 0.0608$  ( $R = 0.0690$ ,  $R_w = 0.0861$  for all 3443 reflections) and  $\Delta/\sigma = 0.01$ . The residual electron

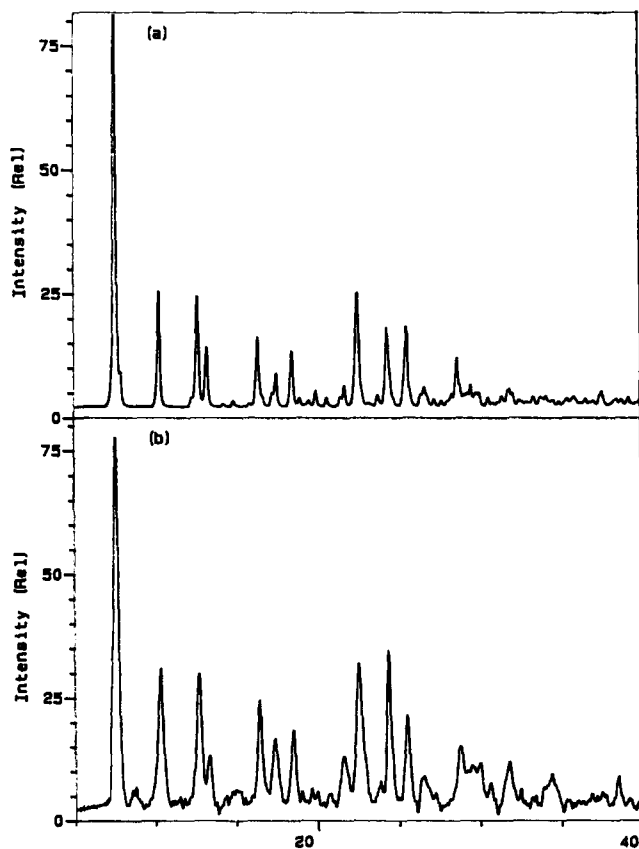


Fig. 5. (a) Theoretical and (b) experimental powder diffraction diagrams of tin phthalocyanine.

density in the final difference Fourier synthesis was within  $0.49\text{--}0.61 \text{ e \AA}^{-3}$ . Scattering factors including corrections for anomalous dispersion were taken from ref. 8. All calculations were performed on an IBM PC/AT. Final atomic parameters and isotropic temperature factors are given in Table 1. Bond lengths and angles are given in Table 2.

### 3. Discussion

#### 3.1. Structure description

An illustration of the independent molecule and the numbering of the atoms is shown in Fig. 1. A view of the stereopacking of the unit cell content is shown in Fig. 2.

The Sn atom in SnPc is coordinated only by four isoindole N atoms. The Sn–N distances, ranging from 2.260(7) to 2.273(5) Å, are about 0.1 Å shorter than in SnPc<sub>2</sub> [7]. Like PbPc [9, 10], the SnPc molecule is not planar. If we take a plane defined by the four isoindole N atoms, it has the equation  $-0.6076X + 0.2861Y + 0.7410Z = -1.3862$ ; the central Sn atom is significantly out of the plane. The deviation of the Sn atom from the above plane is equal to 1.1286 Å. The phenyl rings in SnPc are not perfectly hexagonal, an effect evident also in other phthalocyanines [11–13]. The planes of the four peripheral benzene rings are given in Table 3. The angles of inclination of the planes of benzene rings with respect to the isoindole N plane are equal to 8.0°, 2.0°, 173.0° and 167.4° for rings I, II, III and IV respectively. (The numbering of the benzene rings is given in Fig. 1).

Figure 3 shows the mutual arrangement of molecules seen from the direction parallel to the phthalocyanine plane. One can see that the Sn atom is out of the convex molecular plane. SnPc molecules orient their convex and concave sides alternately. The distances between the planes containing the four isoindole N atoms are 3.556 and 2.869 Å in convex- and concave-type pairs respectively (see Fig. 3). Figure 4 shows the molecular overlap seen from the direction normal to the above plane. In a convex-type pair two molecules (SnPc) mutually overlap only in the region of two benzene rings, while in a concave-type pair considerably more overlap is found. In both cases the Sn atoms are far from each other, the values of Sn–Sn distances being 7.510 and 7.218 Å in convex- and concave-type pairs respectively.

#### 3.2. Data comparison and conclusions

On the basis of the determined atomic positions in the crystal structure of SnPc we calculated the theoretical powder diagram. Figure 5 shows the obtained experimental line positions and intensities for the reaction product of tin with 1,2-dicyanobenzene and the

theoretical ones for SnPc. One can see that the diagrams are quite similar, which proves that SnPc is indeed present in the reaction products of tin or Sn–Au compounds with 1,2-dicyanobenzene.

The analysis performed has shown that 1,2-dicyanobenzene is able to react as well with pure copper or tin as with their gold compounds, although the Au atoms do not react with 1,2-dicyanobenzene under the conditions used. Removal of Cu or Sn atoms from the grain surfaces of the alloys leads to enrichment of the remaining alloy in gold. Moreover, the remaining alloy easily recrystallises, and even pure gold in crystalline form can be present in the reaction products. This leads to the general conclusion that the mobility and ability of inert Au atoms to separate from the alloy plays an essential role in the chemical activity of gold alloys.

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