

attributed (Iida, 1969) to an electron transition from a valence band to a conduction band. Secondly the vibrational bands in the infrared range from 2500 to 700  $\text{cm}^{-1}$  in the solid (KBr discs) are nearly all broadened and those that probably represent skeletal vibrational modes have peaks at frequencies intermediate between those in neutral TCNQ and  $\text{TCNQ}^-$  as shown in Table 6. This provides further evidence for delocalization of charge between the formally neutral TCNQ and  $\text{TCNQ}^-$  in the complex.

Table 6. *Positions of main peaks in the solid state infrared spectra (KBr discs)*

| Probable assignment                 | $\nu$ in complex ( $\text{cm}^{-1}$ ) | $\nu$ in TCNQ ( $\text{cm}^{-1}$ ) | $\nu$ in $\text{TCNQ}^-$ ( $\text{cm}^{-1}$ ) |
|-------------------------------------|---------------------------------------|------------------------------------|---|
| C≡N str.                            | 2199+2167                             | 2228                               | 2195  |
| C=C ring str.                       | 1566                                  | 1545                               | 1581  |
| C=C <i>exo</i> str.                 | 1528                                  | 1545                               | 1509  |
| C-H bend                            | 1328                                  | 1353                               | 1329  |
| C-CN str. ( <i>b<sub>1u</sub></i> ) | 1134                                  | 1126+1114                          | 1186  |

We thank the Science Research Council for the provision of the linear diffractometer, Dr F. R. Ahmed for

the computer programs used and the Director of the Cripps Computing Centre of the University of Nottingham for computing facilities.

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*Acta Cryst.* (1972). **B28**, 1169

## The Crystal and Molecular Structure of Trichlorotrakis-(3-sulphanilamido-6-methoxy-pyridazine)bismuth(III)

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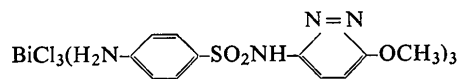
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(Received 21 July 1971)

Trichlorotrakis-(3-sulphanilamido-6-methoxy-pyridazine)bismuth(III),  $\text{BiCl}_3(\text{C}_{11}\text{H}_{12}\text{O}_3\text{N}_4\text{S})_3$ , is trigonal (*R*3) with cell parameters:  $a=18.79(1)$ ,  $c=10.31(1)$  Å,  $Z=3$ . A three-dimensional X-ray analysis, carried out using Patterson and Fourier methods and refined by least-squares methods with photographic data collected at room temperature ( $\text{Cu K}\alpha$ ), shows the Bi to be on a threefold axis surrounded by three chlorine ions [ $\text{Bi}-\text{Cl}=2.529(8)$  Å] and by three nitrogen atoms [ $\text{Bi}-\text{N}=2.90(1)$  Å] and three oxygen atoms [ $\text{Bi}-\text{O}=3.09(2)$  Å] of three sulphanido groups from three different organic molecules. The values of the distances in these contacts indicate that the chlorine atoms are much more strongly bonded to bismuth than the organic molecules.

#### Introduction

Trichlorotrakis-(3-sulphanilamido-6-methoxy-pyridazine)-bismuth(III) was prepared by Adami, Piccinini & Marazzi-Uberti (1961) and introduced in therapy because of its useful pharmaceutical properties, that it is absorbed by the organism more rapidly and completely than the simple mixture of its components. This property could be related to its nature as a coordination compound. The composition, deduced from conventional chemical analysis, corresponds to the formula



in which the stoichiometric ratio is  $\text{BiCl}_3$ : organic molecule = 1:3. But this piece of information is not enough to foresee the coordination around the metal, nor the behaviour of chlorine and of the organic ligand in which more than one possible coordination site is present. These points have been determined from a three-dimensional X-ray crystal analysis which is now reported.

This analysis was started in 1963 and a preliminary report was given at the VI International Congress of the I. U. Cr. (Cavalca, Nardelli, Fava & Giraldi, 1963), but only recently has the complete refinement been made possible by a new set of intensity data.

### Experimental

Trichlorotris-(3-sulphanilamido-6-methoxypyridazine)-bismuth(III) gives small trigonal yellow prisms. Cell constants, determined from rotation and Weissenberg

Table 1. Final atomic fractional coordinates ( $\times 10^4$ ), thermal parameters ( $\text{\AA}^2 \times 10$ ) with *e.s.d.*'s

Temperature factors are given in the form:  $\exp[-\frac{1}{3}(h^2a^*B_{11} + \dots + 2hka^*b^*B_{12} + \dots)]$ .

|       | $x/a$      | $y/b$     | $z/c$      | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{23}$ | $B_{13}$ | $B_{12}$ |
|-------|------------|-----------|------------|----------|----------|----------|----------|----------|----------|
| Bi    | 0          | 0         | 0          | 24 (1)   | 24 (1)   | 21 (1)   | 12 (1)   | 0        | 0        |
| Cl    | -1232 (3)  | -544 (4)  | 1489 (5)   | 28 (2)   | 45 (3)   | 30 (2)   | 18 (2)   | 8 (2)    | 6 (2)    |
| S     | -21 (3)    | 1712 (3)  | -1680 (5)  | 21 (2)   | 24 (2)   | 26 (2)   | 9 (1)    | -1 (1)   | 2 (1)    |
| O(1)  | 673 (8)    | 1577 (10) | -1653 (14) | 22 (5)   | 47 (7)   | 36 (6)   | 21 (5)   | -3 (5)   | 9 (5)    |
| O(2)  | 131 (10)   | 2485 (8)  | -1147 (15) | 44 (8)   | 22 (6)   | 37 (7)   | 10 (5)   | 2 (6)    | 1 (5)    |
| O(3)  | -3808 (9)  | 289 (9)   | -119 (17)  | 29 (6)   | 24 (6)   | 57 (8)   | 9 (5)    | 10 (6)   | 2 (5)    |
| N(1)  | -726 (9)   | 946 (9)   | -963 (16)  | 19 (6)   | 23 (6)   | 32 (7)   | 7 (5)    | -4 (5)   | -4 (5)   |
| N(2)  | -834 (17)  | 1666 (15) | -7266 (21) | 84 (16)  | 55 (12)  | 39 (10)  | 43 (12)  | -13 (10) | -6 (9)   |
| N(3)  | -2881 (10) | -140 (11) | -400 (15)  | 30 (7)   | 43 (8)   | 19 (6)   | 19 (7)   | -2 (5)   | -6 (6)   |
| N(4)  | -2106 (9)  | 91 (10)   | -630 (17)  | 13 (5)   | 21 (6)   | 38 (7)   | 2 (5)    | -5 (5)   | -8 (5)   |
| C(1)  | -1466 (12) | 869 (11)  | -738 (17)  | 32 (8)   | 25 (7)   | 19 (6)   | 14 (6)   | -4 (6)   | -4 (5)   |
| C(2)  | -1668 (12) | 1503 (13) | -550 (20)  | 22 (7)   | 31 (8)   | 33 (8)   | 10 (7)   | -4 (6)   | -10 (7)  |
| C(3)  | -2473 (16) | 1276 (15) | -303 (21)  | 49 (12)  | 43 (11)  | 26 (8)   | 26 (10)  | -6 (8)   | -7 (8)   |
| C(4)  | -3051 (11) | 446 (11)  | -277 (17)  | 22 (7)   | 24 (7)   | 23 (7)   | 14 (6)   | 3 (5)    | 1 (5)    |
| C(5)  | -4404 (23) | -567 (21) | -178 (40)  | 77 (21)  | 56 (17)  | 93 (22)  | 40 (16)  | 23 (18)  | 9 (16)   |
| C(6)  | -306 (12)  | 1679 (12) | -3344 (18) | 28 (8)   | 26 (8)   | 27 (8)   | 8 (6)    | -7 (6)   | 1 (6)    |
| C(7)  | -523 (17)  | 2227 (16) | -3676 (32) | 47 (13)  | 35 (11)  | 77 (17)  | 19 (10)  | -8 (12)  | -10 (11) |
| C(8)  | -705 (14)  | 2219 (14) | -5102 (22) | 39 (10)  | 39 (10)  | 36 (9)   | 21 (9)   | -2 (8)   | 8 (8)    |
| C(9)  | -692 (15)  | 1646 (15) | -5944 (22) | 50 (12)  | 44 (11)  | 31 (9)   | 31 (10)  | -7 (8)   | 3 (8)    |
| C(10) | -477 (17)  | 1077 (16) | -5477 (24) | 54 (13)  | 47 (12)  | 39 (11)  | 27 (11)  | -2 (10)  | -1 (9)   |
| C(11) | -270 (16)  | 1116 (16) | -4130 (24) | 55 (13)  | 49 (12)  | 39 (10)  | 39 (11)  | -8 (9)   | -5 (9)   |

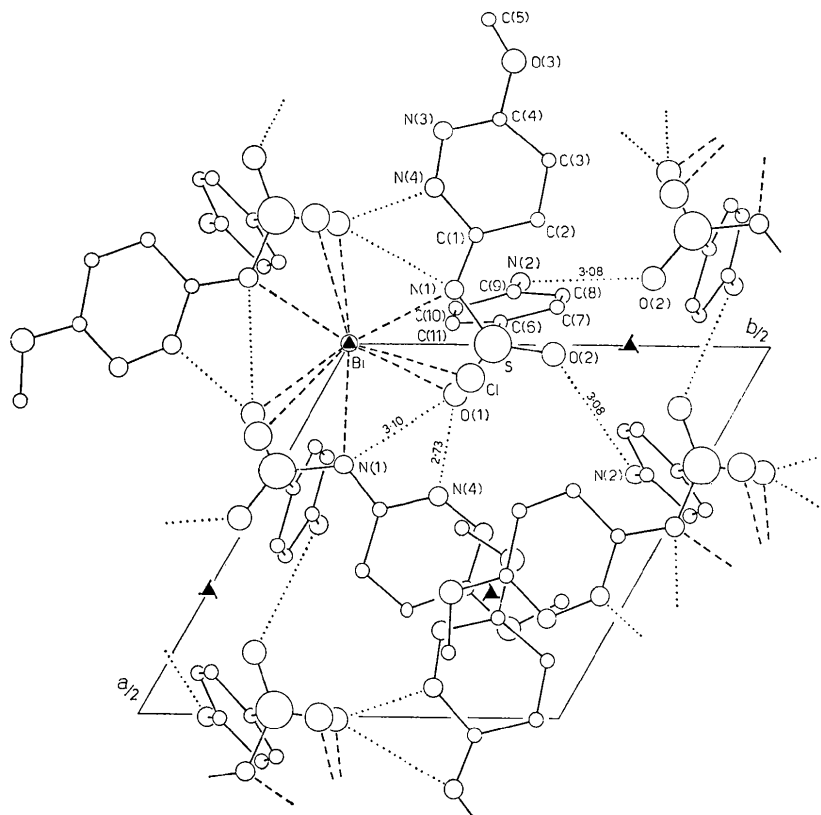


Fig. 1. Projection of the structure along [0001].

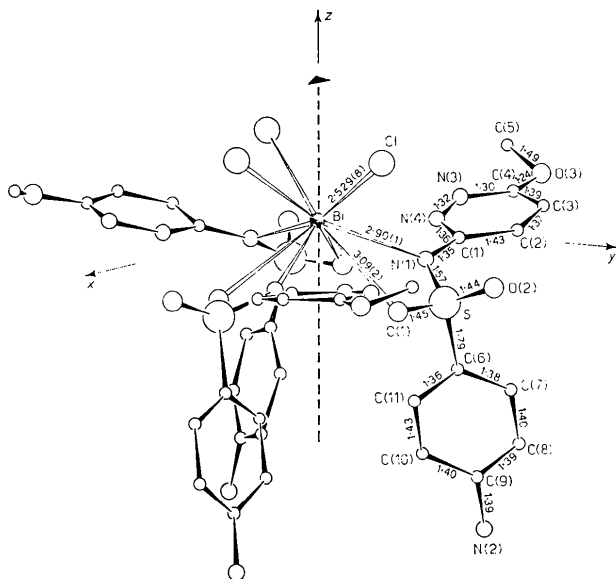
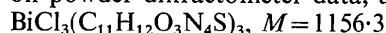


Fig. 2. Clinographic projection of a molecule

photographs and refined by a least-squares procedure on powder diffractometer data, are as follows:



$$a = 18.79(1), c = 10.31(1) \text{ \AA}$$

$$V = 3152 \text{ \AA}^3, Z = 3, D_x = 1.827, D_m = 1.832 \text{ g cm}^{-3}$$

$$\mu = 122.3 \text{ cm}^{-1} (\text{Cu } K\alpha), F(000) = 1176$$

Space group:  $R\bar{3}$  (from systematic absences and structure determination).

The X-ray analysis was carried out, at first, using 953 independent reflexions taken by rotation around [0001]. These data, which correspond to an incomplete reflexion sphere, were used in solving the structure and in a first refinement. However, it was clear from this that the data were not good enough to give acceptable results, in particular with respect to thermal parameters and standard deviations (the main reason probably being the fact that the intensities of the different layers were not properly correlated). A new set of data was therefore collected around the  $b$  axis, taking the Weissenberg photographs of the  $h0.l, \dots, h12.l$  layers. In this way the complete  $\text{Cu } K\alpha$  sphere was obtained (1486 independent reflexions), the intensities being measured photometrically, (15 were too weak to be estimated) and the internal correlation between the intensities of different layers was possible.

The sample used was a nearly spherical fragment of mean radius  $\bar{r} = 0.02$  cm, so the absorption effects were

corrected by assuming the spherical treatment. This second set of data was used in a new refinement which gave more satisfactory results.

The structure amplitudes were derived by the usual formulae, the absolute scale being established first by Wilson's method then by comparison with the calculated values.

### Structure analysis and refinement

A three-dimensional Patterson synthesis calculated with the data collected around [0001] was used to obtain the coordinates for Bi, Cl and S. The contributions of these atoms to the calculated structure factors gave an  $R$  index of 21%, indicating that the interpretation of the Patterson map was correct. The coordinates of the other atoms were obtained with a cycle of Fourier calculations and the residual error index went down to 18%. Refinement was then carried out using Booth's differential synthesis and introducing anisotropic thermal parameters. In this way it was possible to reduce the residual error index to 8.5%. Nevertheless some bond distances between lighter atoms were not satisfactory and exceedingly high thermal parameters and standard deviations were obtained. These results were attributed to the incomplete set of intensity data used in the analysis and to incorrect scaling, so a new set of intensities, covering the complete copper radiation sphere, was collected as indicated in the experimental part and the refinement was resumed starting from the atomic parameters obtained from the last Fourier map. The new cycle of refinement was carried out minimizing, by  $9 \times 9$  block-diagonal least squares, the function  $\sum_{hkl} w_{hkl} [|F_o| - 1/k|F_c|]^2$  in which  $w = |\Delta F|^{-2}$ . At the

end of this refinement the residual error index was  $R = 5.9\%$ , and bond distances and standard deviations had reasonable values. Owing to the presence of the very heavy Bi atom, no attempt was made to locate the hydrogen atoms.

The final atomic parameters with e.s.d.'s are given in Table 1. The  $F_c$  values are calculated with the final parameters using the scattering factors of Cromer & Mann (1968). Copies of the observed and calculated structure factors are available from the authors on request.

The calculations for the first part of the work were performed on the Olivetti Elea 6001/S computer of the 'Centro di Calcolo Elettronico della Università di Parma' using the programs of Nardelli, Musatti, Do-

Table 2. Bond distances and angles with e.s.d.'s

The coordination polyhedron

|         |             |                          |              |                            |              |
|---------|-------------|--------------------------|--------------|----------------------------|--------------|
| Bi-Cl   | 2.529 (8) Å | Cl—Bi—O(1)               | 121.3 (0.3)° | O(1)—Bi—Cl <sup>1</sup>    | 139.8 (0.3)° |
| Bi-O    | 3.09 (2)    | Cl—Bi—N(1)               | 80.8 (0.4)   | O(1)—Bi—O(1 <sup>1</sup> ) | 92.7 (0.4)   |
| Bi-N(1) | 2.90 (1)    | Cl—Bi—Cl <sup>1</sup>    | 87.0 (0.2)   | O(1)—Bi—N(1 <sup>1</sup> ) | 128.3 (0.4)  |
|         |             | Cl—Bi—O(1 <sup>1</sup> ) | 71.3 (0.3)   | N(1)—Bi—Cl <sup>1</sup>    | 162.6 (0.3)  |
|         |             | Cl—Bi—N(1 <sup>1</sup> ) | 80.1 (0.4)   | N(1)—Bi—O(1 <sup>1</sup> ) | 62.2 (0.5)   |
|         |             | O(1)—Bi—N(1)             | 44.0 (0.5)   | N(1)—Bi—N(1 <sup>1</sup> ) | 108.9 (0.5)  |

Table 2 (cont.)

| The pyridazinic ring |            |                  |              |
|----------------------|------------|------------------|--------------|
| C(1)—C(2)            | 1.43 (3) Å | N(4)—C(1)—C(2)   | 115.1 (1.9)° |
| C(1)—N(4)            | 1.36 (3)   | C(1)—C(2)—C(3)   | 118.4 (2.3)  |
| N(4)—N(3)            | 1.32 (3)   | C(2)—C(3)—C(4)   | 118.3 (2.1)  |
| C(2)—C(3)            | 1.37 (4)   | C(3)—C(4)—N(3)   | 124.5 (2.1)  |
| C(4)—N(3)            | 1.30 (3)   | C(4)—N(3)—N(4)   | 116.0 (2.0)  |
| C(4)—C(3)            | 1.39 (4)   | C(1)—N(4)—N(3)   | 127.5 (1.7)  |
| The benzenic ring    |            |                  |              |
| C(6)—C(7)            | 1.38 (3) Å | C(6)—C(11)—C(10) | 119.9 (2.3)° |
| C(6)—C(11)           | 1.36 (3)   | C(11)—C(10)—C(9) | 117.9 (2.4)  |
| C(7)—C(8)            | 1.40 (4)   | C(10)—C(9)—C(8)  | 119.9 (2.1)  |
| C(8)—C(9)            | 1.39 (3)   | C(9)—C(8)—C(7)   | 121.7 (2.2)  |
| C(9)—C(10)           | 1.40 (4)   | C(8)—C(7)—C(6)   | 117.7 (2.5)  |
| C(10)—C(11)          | 1.43 (4)   | C(7)—C(6)—C(11)  | 123.0 (2.2)  |
| N(1)—C(1)            | 1.35 (3)   | S—C(6)—C(11)     | 117.9 (1.6)  |
| C(9)—N(2)            | 1.39 (3)   | C(7)—C(6)—S      | 119.1 (1.9)  |
| C(4)—O(3)            | 1.24 (3)   | C(10)—C(9)—N(2)  | 119.2 (2.3)  |
| C(5)—O(3)            | 1.49 (4)   | N(2)—C(9)—C(8)   | 120.8 (2.3)  |
|                      |            | S—N(1)—C(1)      | 122.1 (1.4)  |
|                      |            | N(1)—C(1)—C(2)   | 128.6 (2.2)  |
|                      |            | N(1)—C(1)—N(4)   | 116.2 (1.7)  |
|                      |            | N(3)—C(4)—O(3)   | 121.4 (2.1)  |
|                      |            | C(3)—C(4)—O(3)   | 114.1 (1.8)  |
|                      |            | C(4)—O(3)—C(5)   | 114.6 (1.7)  |

miano & Andreotti (1964, 1965); for the other calculations, in particular for the least-squares refinement, the CDC 6600 computer of the Consorzio Interuniversitario dell'Italia Nord Orientale was used with the programs written by Immirzi (1967).

### Discussion

From the projection of Fig. 1 and from the values of distances and angles quoted in Table 2, it can be deduced that the compound must be considered as formed by  $\text{BiCl}_3$  molecules loosely bound to the organic molecules which are directed towards the metal by the nitrogen and the oxygen sulphamidic atoms. The Bi—Cl interactions are much stronger than those exerted by the bismuth on the organic molecules.

The coordination polyhedron can be described as a distorted octahedron, formed by three chlorine and three N(1) atoms, with three extra positions occupied by the O(1) atoms. These are roughly at the same level

of the N(1) atoms with respect of the  $c$  axis and form a hexagonal ring having a chair conformation as shown in the clinographic projections of Figs. 2 and 3. The Bi—Cl distance is in good agreement with that (2.52 Å) found in  $\text{Co}(\text{NH}_3)_6\cdot\text{BiCl}_6$  (Atoji & Watanabé, 1952) and is a little longer than the sum of the covalent radii (2.45 Å); the Bi—N(1) and Bi—O(1) distances are much longer than the sum of either the covalent or the ionic radii.

The coordination of the sulphur atom of the sulphanilamide group is tetrahedral; bond distances and angles agree with those found in other sulphanilamides (Table 3), confirming the idea that interactions with the metal are so feeble as to have no influence on its structure.

Both the benzene and pyridazine rings are planar with bond distances and angles in agreement with the expected values. The orientation of these rings is main-

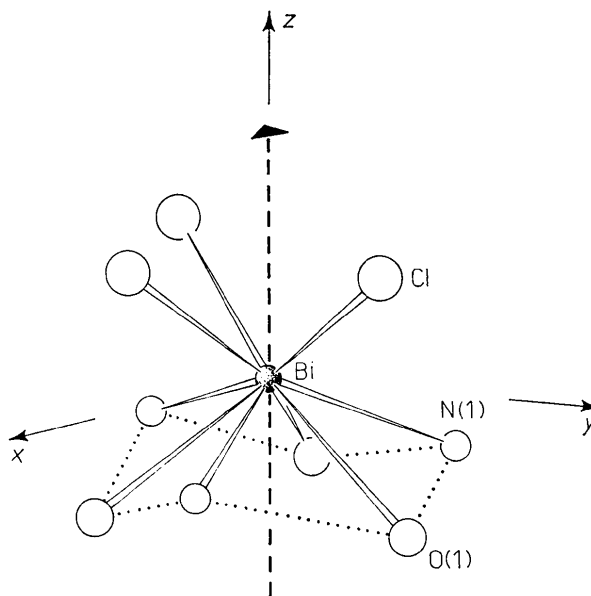


Fig. 3. Clinographic projection of the coordination polyhedron.

Table 3. Bond distances and angles in the sulphanilamide group

|             | Present study | $\alpha$ -Sulphanilamide* | $\beta$ -Sulphanilamide† | 2-Metanilamido-5-Br-pyrimidine‡ |
|-------------|---------------|---------------------------|--------------------------|---------------------------------|
| S—O(1)      | 1.45 (2) Å    | 1.41 Å                    | 1.44 (1) Å               | 1.50 (4) Å                      |
| S—O(2)      | 1.44 (2)      | 1.47                      | 1.44 (1)                 | 1.50 (?)                        |
| S—N(1)      | 1.57 (2)      | 1.61                      | 1.63 (1)                 | 1.75 (4)                        |
| S—C(6)      | 1.79 (2)      | 1.74                      | 1.75 (1)                 | 1.80 (4)                        |
| O(1)—S—O(2) | 115.3 (1.0)°  | 119.0                     | 118.0                    | 132.0                           |
| O(1)—S—N(1) | 104.5 (0.9)   | 106                       | 106                      | 118                             |
| O(2)—S—C(6) | 107.8 (0.9)   | 108                       | 107                      | 114                             |
| N(1)—S—C(6) | 108.6 (1.1)   | —                         | 110                      | 100                             |
| O(2)—S—N(1) | 113.3 (1.0)   | 108                       | 107                      | 97                              |
| O(1)—S—C(6) | 107.0 (0.9)   | 108                       | 107                      | 107                             |

\* O'Connor, B. H. & Maslen, E. N. (1965)

† Alléaume, M. & Decap, J. (1965)

‡ Singer, J. & Fankuchen, I. (1952)

ly determined by packing requirements. The methoxy-pyridazine systems are packed nearly parallel to (0001) around a  $3_1$  axis at  $\frac{1}{3}, \frac{1}{3}, z$  and the aniline groups, which are quite tilted with respect to (0001), are packed around a  $3_2$  axis at  $\frac{1}{3}, 0, z$ . The intermolecular distances less than 3.5 Å are given in Table 4.

Table 4. Intermolecular distances

|                          |            |                          |            |
|--------------------------|------------|--------------------------|------------|
| Cl—N(4)                  | 3.29 (2) Å | O(2)—N(2 <sup>v</sup> )  | 3.08 (4) Å |
| Cl—Cl <sup>i</sup>       | 3.48 (1)   | O(3)—N(3 <sup>iv</sup> ) | 3.30 (2)   |
| Cl—O(1 <sup>i</sup> )    | 3.31 (2)   | O(3)—N(4 <sup>iv</sup> ) | 3.22 (2)   |
| O(1)—N(1 <sup>ii</sup> ) | 3.10 (2)   | O(3)—C(1 <sup>iv</sup> ) | 3.34 (2)   |
| O(1)—N(4 <sup>ii</sup> ) | 2.73 (2)   | O(3)—C(2 <sup>iv</sup> ) | 3.50 (3)   |
| O(1)—C(1 <sup>ii</sup> ) | 3.37 (3)   | O(3)—C(4 <sup>iv</sup> ) | 3.39 (3)   |
| O(1)—C(3 <sup>ii</sup> ) | 3.28 (3)   |                          |            |

|     |                       |                   |                 |
|-----|-----------------------|-------------------|-----------------|
| i   | $\bar{y}$             | $x-y$             | $z$             |
| ii  | $y-x$                 | $\bar{x}$         | $z$             |
| iii | $y-x+\frac{1}{3}$     | $\frac{2}{3}-x$   | $z-\frac{1}{3}$ |
| iv  | $\bar{y}-\frac{1}{3}$ | $x-y+\frac{1}{3}$ | $z+\frac{1}{3}$ |
| v   | $\bar{y}+\frac{1}{3}$ | $x-y+\frac{2}{3}$ | $z+\frac{2}{3}$ |

The authors are indebted to Professor C. Cardani who suggested the research and to the Istituto De Angeli of Milan who kindly gave the crystals of the compound.

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*Acta Cryst.* (1972). B28, 1173

## X-ray Studies of Pyridazino[4,5-*d*]pyridazine Derivatives.

### I. The Structure of 2,6-Dimethyl-4,8-dichloro-2*H*,6*H*-pyridazino[4,5-*d*]pyridazin-1,5-dione

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(Received 21 September 1971)

The crystal structure of 2,6-dimethyl-4,8-dichloro-2*H*,6*H*-pyridazino[4,5-*d*]pyridazin-1,5-dione (DDPPD) has been determined by a three-dimensional Patterson synthesis and refined by the method of least-squares to an *R* value of 0.075. The crystals of DDPPD are monoclinic, space group  $P2_1/n$ , with  $a = 9.189$ ,  $b = 5.546$ ,  $c = 10.230$  Å and  $\beta = 109.82^\circ$ ; the cell content is  $2C_8H_6N_4O_2Cl_2$ . In the molecule of DDPPD the fused ring is approximately planar. Steric hindrance between Cl and O is responsible for the displacement of these atoms from the ring plane and for distortion of the molecule. The packing in the crystal is compact and explains the high melting point (320°C) of the compound.

#### Introduction

The structure determination on 2,6-dimethyl-4,8-dichloro-2*H*,6*H*-pyridazino[4,5-*d*]pyridazin-1,5-dione (DDPPD) was carried out as part of a programme on the derivatives of pyridazino[4,5-*d*]pyridazine (PP), a heterocyclic ring of very high symmetry, synthesized at the Istituto di Chimica Organica of Florence University (Adembri, De Sio, Nesi & Scotton, 1967). The study was undertaken in order to contribute to the knowledge of crystal and molecular structures of heterocyclic compounds with rings containing nitrogen atoms, and to investigate the packing of the molecules in crystals in this series of substances, with reference to

the effect of different molecular substituents on the potential energy. The present paper follows one on the crystal structure of pyridazino[4,5-*d*]pyridazine (Sabelli, Tangocci & Zanazzi, 1969).

The results of the X-ray study on 1,4,5,8-tetramethoxypyridazino[4,5-*d*]pyridazine are reported in the following paper (Fanfani, Zanazzi & Sabelli, 1972).

#### Experimental

Crystals of DDPPD are obtained from benzene as yellowish needles, m.p. 319 to 321°C (Adembri, De Sio, Nesi & Scotton, 1969).

DDPPD crystallizes in the monoclinic system; the