# Crystal and molecular structure of diiodo- $\mathbf{N}, \mathbf{N}, \mathbf{N}^{\prime}, \mathbf{N}^{\prime}$-tetramethylthiuramdisulphidemercury(1i) 

P. T. Beurskens, J. A. Cras, J. H. Noordik and A. M. Spruitt

Department of Inorganic Chemistry, University of Nijmegen, Nijmegen, The Netherlands
(Received 16 February 1970)


#### Abstract

The crystal and molecular structure of diiodo- $\mathrm{N}, \mathrm{N}, \mathrm{N}^{\prime}, \mathrm{N}^{\prime}$-tetramethylthiuramdisulphidemercury(II), $\mathrm{HgI}_{2}\left(\mathrm{~S}_{2} \mathrm{CN}\left(\mathrm{CH}_{3}\right)_{2}\right)_{2}$, has been determined by a three-dimensional X -ray analysis. The compound crystallizes in the monoclinic space group $P 2_{1} / c$ with the unit cell dimensions $a=7.957 \pm 4, b=$ $22 \cdot 639 \pm 7, c=9.956 \pm 6 \AA$ and $\beta=112 \cdot 14 \pm 5^{\circ} ; Z=4$. Intensities were obtained with an automatic diffractometer. The structural parameters were refined by least-squares methods to a conventional $R$ factor of 0.044 for 1294 non-zero observed reflexions. The mercury is in distorted tetrahedral coordination with two iodine and two sulphur atoms. The $\mathrm{Hg}-\mathrm{I}$ distances are $2.654 \pm 2$ and $2 \cdot 661 \pm 2 \AA$; the $\mathrm{Hg}-\mathrm{S}$ distances are $2.651 \pm 7$ and $2.882 \pm 7 \AA$. The thiuramdisulphide ligand consists of two planar units $\mathbf{S}_{2} \mathrm{CNC}_{2}$, nearly perpendicular to each other. Bond distances of the ligand are compared with distances in tetraalkylthiuram disulphide molecules and agree with infrared observations.


## Introduction

In preceding papers, the preparations and properties of diiodo- $\mathrm{N}, \mathrm{N}, \mathrm{N}^{\prime}, \mathrm{N}^{\prime}$-tetrabutylthiuramdisulphidemercury(II) (Brinkhoff et al., 1969) and of the analogous ethyl derivative (Brinkhoff et al. 1970) were reported. The proposed molecular structure was confirmed by an X-ray analysis of the analogous methyl derivative, $\mathrm{HgI}_{2}$ ( $\mathrm{Me}_{4}$ tds).

## Crystal and intensity data

Diiodo- $\mathrm{N}, \mathrm{N}, \mathrm{N}^{\prime}, \mathrm{N}^{\prime}$-tetramethylthiuramdisulphidemercury(II), $\mathrm{HgI}_{2}\left(\mathrm{~S}_{2} \mathrm{CN}\left(\mathrm{CH}_{3}\right)_{2}\right)_{2}, F W$ 694.87, crystallizes in the space group $P 2_{1} / c$ with the unit cell dimensions $a=7.957 \pm 4, b=22.639 \pm 7$, $c=9.956 \pm 6 \AA, \beta=112 \cdot 14 \pm 5^{\circ} ; Z=4$. The prismatic crystals are elongated along $a$. For practical reasons, the unconventional setting $B 2_{1} / d$ was preferred (the transformation matrix to the conventional cell is $00 \mathrm{~T} / 010 / \frac{1}{2} 0 \frac{1}{2}$ ), with needle axis $c$, and the unit cell dimensions $a=18 \cdot 472 \pm 7, b=22.639 \pm$ $7, c=7.957 \pm 4 \AA$ and $\beta=91.47 \pm 5^{\circ} ; V=3326 \pm 4 \AA^{3}, D_{m}=2.76 \pm 3 \mathrm{gcm}^{-3}$ (pycnometer), $Z=8$ and $D_{x}=2.775 \pm 4 \mathrm{gcm}^{-3}$. Zirconium-filtered molybdenum radiation $\lambda($ Mo $K \alpha)=0.7107 \AA$ was used. A crystal of approximately $0.06 \times 0.08 \times 0.38 \mathrm{~mm}^{3}$ was mounted with the needle axis as rotation axis ( $\phi$ axis). The systematic extinctions on Weissenberg and Precession photographs uniquely determined the space group. The cell dimensions were obtained by $\theta, \phi$ and $\chi$ measurements on a Nonius diffractometer; the cell dimensions with their estimated standard deviations are the result of a least-squares treatment of fifteen reflexions in the range $10^{\circ}<\theta<20^{\circ}$.

Intensity data were collected with an automatic Nonius diffractometer, using the moving countermoving crystal method. Deviations from linearity of the scintillation counting equipment were less than $1 \%$. The scan speed was $0.3 \% \mathrm{~min}$. Every 70 min , a reference reflexion was measured to detect fluctuations in the primary beam. Of the 3000 attainable symmetry-independent reflexions (up to $\sin \theta / \lambda=0.595 \AA^{-1}$ ) 1294 reflexions have been measured above background and used for the structure determination. The intensities were corrected for fluctuations in the primary beam and for Lorentz and polarization effects. No absorption correction was applied ( $\mu r_{\text {max }}=0 \cdot 5$; maximum effect upon the intensities: $13 \%$.

## Determination of the structure

The structure was solved by Patterson and Fourier methods; the positions of all atoms (except hydrogen) were located. After successful refinement with isotropic temperature factor parameters, the refinement was continued with anisotropic temperature parameters; the temperature factor was $\exp -\left(h^{2} \beta_{11}+k^{2} \beta_{22}+l^{2} \beta_{33}+2 k l \beta_{23}+2 \ln \beta_{31}+2 h k \beta_{12}\right)$. Because of computer program limitations, the following two procedures were used in turn:
(1) full-matrix refinement of one scale factor and positional and vibrational parameters of all mercury, iodine and sulphur atoms.
(2) full-matrix refinement of the same scale factor and positional and vibrational parameters of all carbon and nitrogen atoms.
After three cycles (1 and 2), all shifts were negligible. The function minimized was $w\left(\left|F_{o}\right|-\left|F_{c}\right|\right)^{2}$, with the weight $w$ for each reflexion as obtained from counting statistics. The atomic scattering factors used were those of the neutral atoms corrected for anomalous scattering ( $\Delta f^{\prime}$ ), with data from the International Tables (1962). The final conventional $R$ factor is 0-044.

The final difference Fourier map showed some maxima of $0.7 \mathrm{e}^{\AA^{-3}}$ around the mercury position, and on the mercury position a minimum of about $-0.5 \mathrm{e}^{-3}$. At distances varying from 0.7 to $1.5 \AA$ to the methylcarbon positions, a number of maxima of height $0.3-0.5 \mathrm{e} \AA^{-3}$ were found but none of these could be interpreted clearly as hydrogen.

Calculations were performed on an IBM 360/50 computer, using programs written by Busing et al. (1962), Pippy \& Ahmed (1967), Beurskens et al. (1969) and Beurskens (1968).

## Description of the molecule

The atomic parameters are given in table 1, and the structure is illustrated in Fig. 1. Bond distances and angles are given in Fig. 2; the shortest $S-S$ van der Waals contact is 3.78(1) $\AA$.

The coordination of mercury is shown in Fig. 3. The mercury atom is equidistant to the two iodine and the $\mathrm{S}(1)$ atoms ( $2.66 \AA$ ), and is only $0.305 \pm 1 \AA$ out of the plane of these three atoms. The $\mathrm{Hg}-\mathrm{S}(4)$ bond ( $2.88 \AA$ ) is significantly longer and nearly perpendicular ( $84^{\circ}$ ) to this plane. A similar geometry was found in the compound $\left[\mathrm{S}\left(\mathrm{CH}_{3}\right)_{3}\right]_{2} \mathrm{HgI}_{4}$ (Fenn, 1966), with three $\mathrm{Hg}-\mathrm{I}$ bonds of $2 \cdot 70 \AA$ (average) and one $\mathrm{Hg}-\mathrm{I}$ bond of $2.80 \AA$. The $\mathrm{Hg}-\mathrm{S}(4)$ distances in other tetrahedrally coordinated mercury compounds are, for example, $2.33 \AA$ in HgS (metacinnabar) (Aurivillius, 1950) and $2.61 \AA$ in $\mathrm{HgCl}_{2}$ -1,3,5-trithian (Costello et al., 1966). The $\mathrm{S}-\mathrm{Hg}-\mathrm{S}$ and $\mathrm{I}-\mathrm{Hg}-\mathrm{I}$ angles agree within $3^{\circ}$ with the relationship between coordination angles given by Cheung \& Sim (1965).

The thiuramdisulphide ligand contains two planar groups $\mathbf{S}_{\mathbf{2}} \mathrm{CNC}_{2}$. The equation of the least squares plane through $\mathrm{S}(1) \mathrm{S}(2) \mathrm{C}(1) \mathrm{N}(1) \mathrm{C}(3) \mathrm{C}(4)$ is

$$
0.0308 X+0.5997 Y+0.7997 Z-0.3465=0
$$

with the deviations from the plane

$$
\begin{array}{ll}
S(1):-0.003(7) & N(1):-0.01(2) \\
S(2): 0.005(7) & C(3):-0.04(2) \\
C(1):-0.03(2) & C(4): 0.08(2)
\end{array}
$$

Table 1. Atomic parameters for $\mathrm{HgI}_{2}\left(\mathrm{Me}_{4} \mathrm{tds}\right)$ and standard deviations

|  | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{33}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Hg | 0.0703(1) | $0 \cdot 1690 \cdot(1)$ | 0.1030(2) | 0.0035(1) | 0.0020(1) | 0-0198(3) | -0.0004(1) | 0.0022(1) |  |
| I(1) | $-0.0418(1)$ | $0 \cdot 1271(1)$ | 0.2697(3) | 0.0032(1) | 0-0033(1) | $0.0247(6)$ | $-0.0001(1)$ | 0.0022(1) | $\begin{array}{r} -0.0009(1) \\ 0.0025(1) \end{array}$ |
| I(2) S(1) | $0.1487(1)$ | $0 \cdot 2660(1)$ | 0.0627(3) | $0.0051(1)$ | 0.0019(1) | $0.0272(6)$ | -0.0008(1) | 0-0009(2) | $-0.0008(1)$ |
| S(1) S(2) | 0.0703(3) | 0.1059(3) | -0.1776(9) | $0.0026(2)$ | $0.0031(2)$ | 0.0170(18) | $-0.0003(2)$ | 0.0001(6) | -0.0008(1) |
| S(2) S(3) | $0.2306(3)$ $0.1817(4)$ | $0 \cdot 0795(3)$ | $-0.1370(9)$ $-0.0241(10)$ | $0.0029(3)$ $0.0056(3)$ | 0.0033(2) | 0.0216(20) | 0.0007(2) | 0.0007(6) | $0 \cdot 0017(5)$ |
| S(4) | 0.1896(3) | 0.1038(3) | -0.0241(10) | $0 \cdot 0056(3)$ | $0 \cdot 0019(2)$ | $0 \cdot 0210(21)$ | 0.0007(2) | $0 \cdot 0012(7)$ | $-0.0004(5)$ |
| C(1) | 0.1579(10) | 0.1242(9) | -0.2202(28) | 0.0019(8) | $0.0019(2)$ $0.0022(6)$ | $0.0200(19)$ $0.0061(56)$ | $0.0001(2)$ $-0.0001(6)$ | $-0.0034(6)$ | -0-0002(5) |
| N(1) | 0-1756(9) | 0.1684(8) | -0.3188(23) | $0.0036(8)$ | $0.0015(4)$ | $0.0061(56)$ $0.0126(49)$ | $-0.0001(6)$ $-0.0018(6)$ | $-0.0017(18)$ $0.0016(16)$ | $-0.0028(16)$ $-0.0012(14)$ |
| C(2) | $0 \cdot 1662(11)$ | $0 \cdot 0328(10)$ | 0-1949(28) | $0.0025(9)$ | $0.0026(7)$ | 0.0037(60) | $0.0014(7)$ | $0 \cdot 0016(16)$ $-0.0002(19)$ | -0-0012(14) |
| N(2) | $0 \cdot 1314(9)$ | $-0.0046(10)$ | 0.2809(28) | 0.0016 (7) | $0.0034(7)$ | $0 \cdot 0148(57)$ | $0.0004(6)$ | 0.0012(17) | $0 \cdot 0048(18)$ |
| C(3) | $0 \cdot 2536(12)$ | $0 \cdot 1806(10)$ | -0.3473(28) | 0.0036(10) | $0 \cdot 0026(8)$ | 0-0139(63) | -0.0016(7) | $0 \cdot 0033(21)$ | $0 \cdot 0012(17)$ |
| C(4) | $0 \cdot 1173(12)$ | $0 \cdot 2051(11)$ | $-0.4065(33)$ | $0.0046(11)$ | $0.0022(7)$ | $0.0302(79)$ | $0.0030(7)$ | -0.0061(25) | -0.0017(18) |
| C(5) C(6) | $0 \cdot 1117(13)$ | $0.0086(8)$ | 0.4544 (33) | $0.0027(9)$ | $0.0039(8)$ | $0.0106(67)$ | $0.0014(7)$ | $-0.0001(21)$ | 0.0025(20) |
| C(6) | $0 \cdot 1142(12)$ | -0.0643(9) | $0 \cdot 2156(36)$ | $0.0037(10)$ | 0-0006(5) | 0.0472(97) | $-0-0011(6)$ | 0-0012(25) | $-0.0028(19)$ |

The key to the atomic numbering is given in Figure 2. The general positions for space group $B 2_{1} / d$ are: $\left(0,0,0 ; \frac{1}{2}, 0, \frac{1}{2}\right) \pm\left(x, y, z ; \frac{1}{4}+x, \frac{1}{2}-y, \frac{1}{4}+z\right)$. The positions for the $P 2_{1} / c$ setting are given by the transformation matrix 10I/010/200.


Fig. 1. Projection of $\mathrm{HgI}_{2}\left(\mathrm{Me}_{4} \mathrm{tds}\right)$ on (101).



Fig. 2. Bond distances and angles in $\mathrm{HgI}_{2}\left(\mathrm{Me}_{4} \mathrm{tds}\right)$ and standard deviations. The bond angles $\mathrm{I}_{1}-\mathrm{Hg}-\mathrm{S}_{4}\left(102 \cdot 1 \pm 2^{\circ}\right)$ and $\mathrm{I}_{1}-\mathrm{Hg}-\mathrm{S}_{1}\left(109 \cdot 4 \pm 2^{\circ}\right)$ are not given in the figure.

# diIODo- $\mathbf{N}, \mathbf{N}, \mathbf{N}^{\prime}, \mathrm{N}^{\prime}$-TETRAMETHYLTHIURAMDISULPHIDEMERCURY(II) 



Fig. 3. Coordination of the Hg atom. Projection parallel to the plane through $\mathrm{I}(1), \mathrm{I}(2)$ and $\mathrm{S}(1)$.

The plane through $\mathrm{S}(3) \mathrm{S}(4) \mathrm{C}(2) \mathrm{N}(2) \mathrm{C}(5) \mathrm{C}(6)$ is given by

$$
0.8852 X-0.3523 Y+0.3038 Z-2.8330=0
$$

with the deviations from the plane

$$
\begin{array}{ll}
S(3): 0.001(7) & N(2): 0.02(2) \\
S(4): 0.002(7) & C(5):-0.03(2) \\
C(2):-0.06(2) & C(6): 0.06(2)
\end{array}
$$

The dihedral angle between these planes is $86 \cdot 6^{\circ}$. The atom $S(2)$ is situated in both planes, and the dihedral $\mathbf{C}-S-S-C$ angle is $89.2^{\circ}$.

In Table 2, the geometry of the thiuramdisulphide ligand in $\mathrm{HgI}_{2}\left(\mathrm{Me}_{4} \mathrm{tds}\right)$, is compared with the geometry of tetramethylthiuramdisulphide ( $\mathrm{Me}_{4} \mathrm{tds}$ ) (Marøy, 1965) and tetraethylthiuramdisulphide ( $\mathrm{Et}_{4} \mathrm{tds}$ ) (Karle, Estlin and Britts, 1967). The observed $\mathbf{C}-\mathrm{N}$ distances are not conclusive with respect to the increase of the $\mathbf{C}-\mathrm{N}$ bond order as indicated by infrared and nmr measurements. The difference in the C-S distances agree with the infrared spectra (Brinkboff et al., 1970).

Table 2. Comparison of the geometry in thiuramdisulphide

|  | $\mathrm{HgI}_{2}\left(\mathrm{Me}_{4} t d s\right)$ | $\mathrm{Me}_{4} t d s$ | $\mathrm{Et}_{4} t d s$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{C}(1)-\mathrm{N}(1), \mathrm{C}(2)-\mathrm{N}(2)$ | $1 \cdot 27,1 \cdot 32 \AA$ | $1 \cdot 31 \AA$ | $1 \cdot 33,1 \cdot 36 \AA$ |
| $\mathrm{C}(1)-\mathrm{S}(1), \mathrm{C}(2)-\mathrm{S}(4)^{*}$ | $1 \cdot 71,1 \cdot 72 \AA$ | $1 \cdot 61 \AA$ | $1 \cdot 66,1 \cdot 63 \AA$ |
| $\mathrm{~S}(2)-\mathrm{S}(3)$ | $2 \cdot 03 \AA$ | $2 \cdot 00 \AA$ | $2 \cdot 00 \AA$ |
| Dihedral $\mathrm{C}(1)-\mathrm{S}(2)-\mathrm{S}(3)-\mathrm{C}(2)$ angle | $89 \cdot 2^{\circ}$ | $88^{\circ}$ | $96 \cdot 4^{\circ}$ |

* $\mathrm{C}=\mathrm{S}$ bond in $\mathrm{Me}_{4} \mathrm{tds}$ and $\mathrm{Et}_{4} \mathrm{tds}$.

The authors are grateful to Professor J. J. Steggerda for his continuous interest, and to Mr W. P. J. H. Bosman and Mr J. M. M. Smits for valuable assistance.

## References

Aurivillius, K. L. (1950) Acta Chem. Scand. 4, 1413.
Beurskens, P. T. (1968) A Fourier Computer Program (unpublished).
Beurskens, P.T., Noordik, J.H. \& Bosman, W. P.J.H. (1969) Fortran Computer Programs for Cell Dimensions, Setting Angles and Data Reduction for the Nonius Automatic Diffractometer (unpublished).
Brinkhoff, H. C., Cras, J. A., Steggerda, J. J. \& Willemse, J. (1969) Rec. Trav. Chim. 88, 633.
Brinkhoff, H. C., Grotens, A. M. \& Steggerda, J. J. (1970) Rec. Trav. Chim. 89, 11.

Busing, W. R., Martin, K. O. \& Levy, H. A. (1962) Fortran Least Squares Program (ORFLS).
Cheung, K. K. \& Sim, G. A. (1965) J. Chem. Soc. 5988.
Costello, W. R., McPhail, A. P. \& Sim, G. A. (1966) J. Chem. Soc. (A), 1190.
Fenn, R. H. (1966) Acta Cryst. 20, 24.
Karle, I. L., Estlin, J. A. \& Britts, K. (1967) Acta Cryst. 22, 273.
Marøy, K. (1965) Acta Chim. Scand. 19, 1509.
Pippy, M. E. \& Ahmed, F. R. (1967) Scan of Interatomic Distances and Angles (NRC-12), Mean Plane (NRC22).

National Lending Library Supplementary Publication No. 60006 contains 4 pages of structure factor tables on 1 microfiche.

