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The Crystal Structure of Mercury Tetrathiocyanate–Copper Diethylenediamine, $[Hg(SCN)_4][Cu(en)_2]$*

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Crystals of $[Hg(SCN)_4][Cu(en)_2]$ are monoclinic with:

$$a = 7{\cdot}51, b = 18{\cdot}03, c = 14{\cdot}20 \text{ Å}, \beta = 96° \ 32'.$$

The space group is $P2_1/c$ with four molecules per unit cell containing four units of $[Hg(SCN)_4][Cu(en)_2]$.

The structure was determined by two- and three-dimensional Fourier methods, using the heavy-atom technique. The two-dimensional analyses established the positions of the Hg, Cu and the four S atoms, and then from three-dimensional Fourier syntheses more accurate co-ordinates for all the atoms were obtained. The results are as follows: The four S atoms were found to be tetrahedrally situated about the Hg atom but the thiocyanate groups themselves, which are placed at an angle to the Hg–S bonds, do not follow the tetrahedral arrangement of the S atoms. The (SCN) groups appear to be kinked at the C atom. Mean values of bond lengths and bond angles in the $Hg(SCN)_4$ unit are:

$$\text{Hg–S} = 2{\cdot}55 \text{ Å}, \ \text{S–C} = 1{\cdot}57 \text{ Å}, \ \text{C–N} = 1{\cdot}34 \text{ Å}.$$
$$\text{S–Hg–S} = 109° \ 16', \ \text{Hg–S–C} = 102° \ 5', \ \text{S–C–N} = 163° \ 12'.$$

The $Cu(en)_2$ groups form two five-membered non-planar rings symmetrically placed about each copper atom, but with different orientation for the two crystallographically different copper atoms. Mean dimensions of the Cu(en) rings are: Cu–N = 2·07 Å, N–C = 1·41 Å, C–C = 1·53 Å, with N–Cu–N angle of about 80°.

Two N atoms of the (SCN) groups are co-ordinated to each Cu atom, thus giving it a total of sixfold co-ordination. This co-ordination direction is approximately at right angles to the plane containing the Cu and the amino N atoms.

1. Introduction

The spatial distribution of the mercury valency bonds in the mercuric tetrathiocyanates has not been studied with any certainty. In 1945 Prof. W. Wardlaw, who posed the problem, kindly supplied us with crystals of the four compounds $Co[Hg(SCN)_4]$, $Ni[Hg(SCN)_4]$, $[Cu(en)_2][Hg(SCN)_4]$ and $[Cu(pyr)][Hg(SCN)_4]$ which were prepared at the Chemistry Department of Birkbeck College. There was also the question whether the sulphurs or some other atoms of the thiocyanate groups were attached to the mercury atom. The cobalt compound with space group $I\bar{4}$ (Jeffery, 1947) implied that the four thiocyanate groups in this compound were tetrahedrally arranged about the mercury atom, and from two-dimensional Fourier syntheses it was suggested that the sulphur atoms were themselves tetrahedrally situated about the mercury atom. This analysis, however, was not carried far enough to give reliable information about the carbon and nitrogen atoms of the (SCN) groups.

The crystals of the other three compounds were of a lower symmetry and gave no clue to the arrangement of the (SCN) groups about the mercury atoms. The $Cu(en)_2$-compound, however, offered the opportunity of investigating at the same time the stereochemistry of copper-diethylenediamine itself, and a detailed X-ray crystal structure analysis of this compound was accordingly undertaken. A preliminary account has already appeared (Scouloudi & Carlisle, 1950).

2. Preliminary investigation: experimental

The crystals of $[Hg(SCN)_4][Cu(en)_2]$, which are deep purple, crystallize from acetone and water in well developed monoclinic prismatic plates with forms {011}, {110}, {101} and with {010} dominating.

The birefringence is positive with $\gamma \| b$ and β lying at about 24° to the c axis in the obtuse angle. $2V \simeq 65°$ (in glycerin). Dichroism is observed on {010}, the colour changing from light mauve to dark purple when the vibration direction is normal to α and β respectively.

Oscillation and Weissenberg photographs taken with copper radiation ($\lambda = 1{\cdot}542$ Å) gave

$$a = 7{\cdot}51_0, \ b = 18{\cdot}03_2, \ c = 14{\cdot}20_1 \text{ Å}, \ \beta = 96° \ 32' \pm 1',$$
$$V = 1910{\cdot}60 \text{ Å}^3.$$

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* This paper is an abridged version of a thesis approved by the University of London for the degree of Ph.D.

The density by flotation was $2{\cdot}12_7$ g.cm.$^{-3}$. The molecular weight, calculated from $HgCuS_4N_8C_8H_{16}$, is 616·56; hence there are four (calculated 3·96) molecules per unit cell containing four units of $Hg(SCN)_4$ and $Cu(en)_2$. $F(000) = 293$ per molecule. $\mu_l = 211{\cdot}4$ cm^{-1}.

Among the X-ray reflexions systematic absences occurred for reflexions of the type ($0k0$) when k is odd and ($h0l$) when l is odd; so the space group is $P2_1/c$.

Altogether 1160 (hkl) reflexions were used in the determination of the structure; these were recorded from a series of equi-inclination Weissenberg photographs taken about the three principal axes. In order to reduce absorption errors, small specimens were used with cross-sections ($0{\cdot}16\times0{\cdot}07$) mm.^{2}, ($0{\cdot}16\times0{\cdot}13$) mm.^{2} and ($0{\cdot}07\times0{\cdot}07$) mm.^{2} for the a, b and c axes respectively, and were completely immersed in the X-ray beam.

The multiple-film technique (Robertson, 1943) was employed and in some cases a thin sheet of aluminium foil was inserted between the second and third films. The intensities of the X-ray reflexions were estimated visually, using an arbitrary intensity scale.

In correlating the intensities of the X-ray reflexions recorded on all sets of films, the following two factors were taken into consideration: (a) the variation in size of spots on Weissenberg photographs other than those from the zero-level, and (b) the rotation factor. The former effect, which arises because of the divergence of the X-ray beam together with the motion of the film (Buerger, 1942), causes certain reflexions on one half of the films with $\mu \neq 0$ to be recorded on a smaller area (compacted spots) than those on the other half of the film, where the spots are drawn out into a streak. Hence, when reflexions occurring on both halves of the films had to be used, because $F(hkl) \neq F(hk\bar{l})$, an empirical correction was applied in the following way:

Reflexions of the type $hk0$ or $0kl$, lying on the axes, which on space-group considerations would have been identical for both positive and negative values of h or l, were estimated from the upper and lower halves of each layer-line photograph and the ratio $I_{\text{lower}}/I_{\text{upper}}$ for each pair of reflexions of the above type was plotted as a function of $\sin\theta$ separately for every layer line. As can be seen from Fig. 1, this ratio increased with the layer line level n for values of $\sin\theta < 0{\cdot}7$. For the same layer line (constant μ angle), however, the values of the ratio decreased with $\sin\theta$, all tending to unity for $\sin\theta \geqslant 0{\cdot}7$. In this way every hkl reflexion on one half of each film was multiplied by the appropriate factor corresponding to its $\sin\theta$ value.

Rotation-factor corrections were obtained from the data given by Tunell (1939) for equi-inclination Weissenberg photographs.

After applying these two corrections, satisfactory agreement was obtained between measured intensities of identical reflexions recorded on different layer lines and with crystals oscillated about different axes.* The measured intensities were finally corrected for the Lorentz and polarization factors, using a graphical method devised by Goldschmidt & Pitt (1948), and a set of coefficients proportional to $F^2(hkl)$ was obtained.

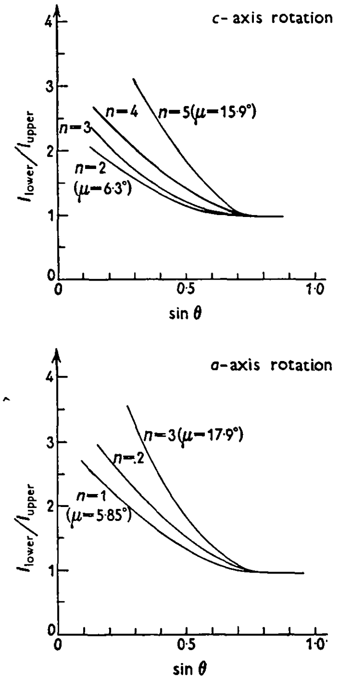

Fig. 1. Curves showing the correlation of intensities of reflexions occurring on the upper and lower halves of each n-level Weissenberg photograph.

3. Determination of the structure

The structure has been determined by making use of the heavy-atom technique (Robertson & Woodward, 1940). The difficulties of this method are well known (Cox, 1938), and we did in fact find that it was not possible to locate from the projections the light carbon and nitrogen atoms.

The space group $P2_1/c$ requires four general positions with co-ordinates x, y, z; $x, \frac{1}{2}-y, \frac{1}{2}+z$; $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; $\bar{x}, \bar{y}, \bar{z}$; or there can be four twofold special positions at $0, 0, 0$ and $0, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and $\frac{1}{2}, 0, 0$; $0, 0, \frac{1}{2}$ and $0, \frac{1}{2}, 0$; $\frac{1}{2}, 0, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, 0$. The $[Hg(SCN)_4]$ group does not possess a centre of symmetry and it is possible that the four mercury atoms are in general positions. The two ethylenediamine groups, however, are likely to be chelated to the copper atom, through the nitrogen atoms, to form with it two symmetrically

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* Owing to the large number of the recorded planes, no attempt was made to correct the intensities for absorption. Although this effect could not be negligible, inspection of the X-ray photographs showed a rather uniform distribution of the intensity, viewed visually, inside the area occupied by each reflexion.

arranged five-membered rings. In this case, the copper atoms could be placed at special positions.

From Patterson projections on (100), (010) and (001) it was possible to locate the mercury atom at $x = 0{\cdot}133$, $y = 0{\cdot}225$, $z = 0{\cdot}285$. The three Patterson projections were also consistent with the four copper atoms lying at the centres of symmetry: $\frac{1}{2}, 0, 0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, 0, \frac{1}{2}$ and $\frac{1}{2}, \frac{1}{2}, 0$.

(a) *Two-dimensional Fourier syntheses*

Assuming the above positions of mercury and copper, the co-ordinates of the sulphur atoms were obtained from Fourier projections on (100), (010) and (001). The final projection on (100) is shown in Fig. 2.

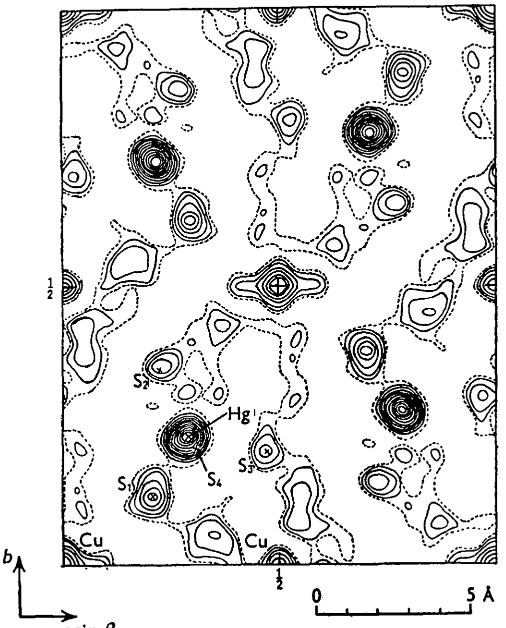

Fig. 2. Electron-density projection on (100) based on the contribution of the mercury, copper and four sulphur atoms with coordinates as shown in the figure. Contours at arbitrary intervals.

The final co-ordinates of the mercury, copper and sulphur atoms, as obtained from the projections (Table 1) gave the following discrepancy factors $R = \Sigma||F_o|-|F_c|| \div \Sigma|F_o|$:

$$R_{(0kl)} = 0{\cdot}34,\ R_{(h0l)} = 0{\cdot}43,\ R_{(hk0)} = 0{\cdot}33\ .$$

These values were considered satisfactory to proceed to three-dimensional Fourier syntheses.

Table 1. *Co-ordinates obtained from the two-dimensional analyses*

Atom	x	y	z
Hg	0·133	0·227	0·292
S_1	0·020	0·120	0·210
S_2	0·020	0·302	0·230
S_3	0·053	0·202	0·475
S_4	0·493	0·203	0·306
½(Cu)	½	0	0
½(Cu)	½	0	½

(b) *Three-dimensional Fourier syntheses*

The 1160 recorded *hkl* reflexions were used to evaluate electron-density sections parallel to the three main axes. Space does not permit a presentation of all these electron-density sections—a detailed description of the work can be found in a Thesis (Scouloudi, 1951). We shall confine ourselves here to the results. The final co-ordinates of all the atoms are given in Table 2.

Table 2. *Final co-ordinates of all the atoms derived from three-dimensional Fourier syntheses*

Atom	x	y	z
Hg	0·133	0·228	0·287
S_1	−0·012	0·116	0·203
S_2	0·049	0·355	0·230
S_3	0·046	0·206	0·456
S_4	0·479	0·208	0·298
C_1	−0·038	0·066	0·289
C_2	0·160	0·410	0·310
C_3	0·135	0·277	0·490
C_4	0·439	0·123	0·302
N_1	−0·057	0·036	0·377
N_2	0·286	0·446	0·362
N_3	0·291	0·296	0·537
N_4	0·469	0·051	0·318
N_5	0·633	0·097	0·047
N_6	0·717	0·018	−0·081
C_5	0·741	0·130	−0·018
C_6	0·863	0·068	−0·047
N_5'	0·590	0·088	0·068
N_6'	0·380	−0·026	0·128
C_5'	0·474	0·083	0·135
C_6'	0·511	0·008	0·187
N_7	0·704	0·072	0·521
N_8	0·358	0·079	0·569
C_7	0·598	0·133	0·545
C_8	0·502	0·112	0·629

The $Hg(SCN)_4$ *group*.—The four sulphur atoms were found to be tetrahedrally arranged about the mercury atom at a mean distance of 2·56 Å and at a mean S–Hg–S angle of 109° 16′. Individual bond lengths

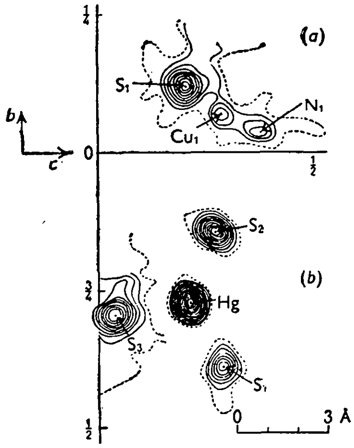

Fig. 3. Part of the electron density section at $x = 0{\cdot}94$ showing (*a*) one (SCN)-group from the molecule at x, y, z and (*b*) the mercury and three of the sulphur atoms from the molecule at $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$. Contours at arbitrary intervals.

and bond angles for the HgS_4 tetrahedron are shown in Fig. 7(*a*). The thiocyanate groups lie at an angle from the corresponding Hg–S bonds and the angle at the sulphur atoms has a mean value of 102° 5′. There is a possibility that the thiocyanate groups in this structure are non-linear (see Fig. 3) and this was seemingly confirmed from other sections. We have to bear in mind, however, that the peak positions of the light atoms can be affected by the diffraction rings of the heavier atoms (Bragg & West, 1930; James, 1948; Robertson & Woodward, 1940) and so these conclusions should be accepted with some caution. If we assume the thiocyanates to be S–C–N,* the angle at the carbon atom has a mean value of about 163° and the mean S–C and C–N distances were found to be 1·57 and 1·33 Å respectively. The four thiocyanate groups do not follow the tetrahedral arrangement of the sulphurs about the mercury atom but take up unsymmetrical positions satisfying the structural features of geometrical packing and charge neutralization (Fig. 6(*a*)). The observed bond lengths and bond-angles in the $Hg(SCN_4)$ group can be seen in Fig. 7.

The $[Cu(en)_2]$ *group*.—As the copper atoms lie at the twofold special positions, each pair of $Cu(en)_2$ has an orientation independent of the other. Two ethylenediamine groups are co-ordinated to each copper atom through the amino-nitrogens, thus forming two five-membered rings symmetrically arranged about the copper atoms. These rings are non-planar (see Figs. 4 and 5) and only the amino-nitrogens lie on the same plane with the copper atom at a nearly square co-ordination, but the two carbons in each ring lie out

Table 3. *Bond lengths and bond angles*

(*a*) $Hg(SCN)_4$ group

$Hg–S_1$	= 2·53 Å	$S_1–Hg–S_2$	= 120° 12′
$Hg–S_2$	= 2·49	$S_1–Hg–S_3$	= 100 1
$Hg–S_3$	= 2·59	$S_1–Hg–S_4$	= 106 54
$Hg–S_4$	= 2·61	$S_2–Hg–S_3$	= 111 11
$S_1–C_1$	= 1·55	$S_2–Hg–S_4$	= 111 9
$S_2–C_2$	= 1·66	$S_3–Hg–S_4$	= 106 8
$S_3–C_3$	= 1·50	$Hg–S_1–C_1$	= 100 21
$S_4–C_4$	= 1·56	$Hg–S_2–C_2$	= 103 49
$C_1–N_1$	= 1·38	$Hg–S_3–C_3$	= 91 0
$C_2–N_2$	= 1·31	$Hg–S_4–C_4$	= 86 44
$C_3–N_3$	= 1·33	$S_1–C_1–N_1$	= 167 15
$C_4–N_4$	= 1·33	$S_2–C_2–N_2$	= 163 42
		$S_3–C_3–N_3$	= 135 58
$S_1–N_1$	= 2·91 (inter)	$S_4–C_4–N_4$	= 158 41
$S_2–N_2$	= 2·93 (inter)		
$S_3–N_3$	= 2·62 (inter)		
$S_4–N_4$	= 2·85 (inter)		

(*b*) Copper–ethylenediamine ring
$(Cu–NH_2–CH_2–CH_2–NH_2–Cu)$
Groups at ½, 0, 0

(*a*)		(*b*)	
$Cu–N_5$	= 2·08 Å	$Cu–N_5'$	= 1·94 Å
$Cu–N_6$	= 2·13	$Cu–N_6'$	= 2·17
$N_5–C_5$	= 1·41	$N_5'–C_5'$	= 1·36
$N_6–C_6$	= 1·45	$N_6'–C_6'$	= 1·36
$C_5–C_6$	= 1·53	$C_5'–C_6'$	= 1·55
$N_5–Cu–N_6$	= 70° 31′	$N_5'–Cu–N_6'$	= 85° 12′
$N_5–C_5–C_6$	= 105 30	$N_5'–C_5'–C_6'$	= 107 15
$N_6–C_6–C_5$	= 95 23	$N_6'–C_6'–C_5'$	= 91 18
$Cu–N_5–C_5$	= 116 47	$Cu'–N_5'–C_5'$	= 94 34
$Cu–N_6–C_6$	= 119 13	$Cu'–N_6'–C_6'$	= 94 26

Group at ½, 0, ½

$Cu–N_7$	= 2·00 Å	$N_7–Cu–N_8$	= 84° 54′
$Cu–N_8$	= 2·09	$N_7–C_7–C_8$	= 106 40
$N_7–C_7$	= 1·43	$N_8–C_8–C_7$	= 92 2
$N_8–C_8$	= 1·43	$Cu–N_7–C_7$	= 95 36
$C_7–C_8$	= 1·50	$Cu–N_8–C_8$	= 99 52

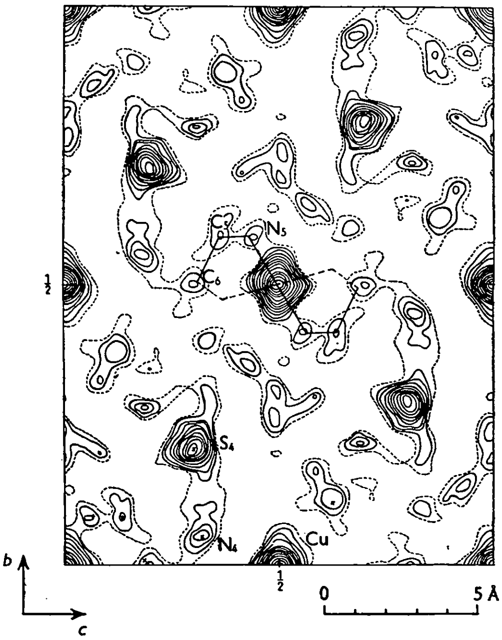

Fig. 4. Electron-density section at $x = \frac{1}{2}$. The $(en)_2$ groups attached to the copper atoms at ½, ½, ½ are outlined. Contours at arbitrary intervals.

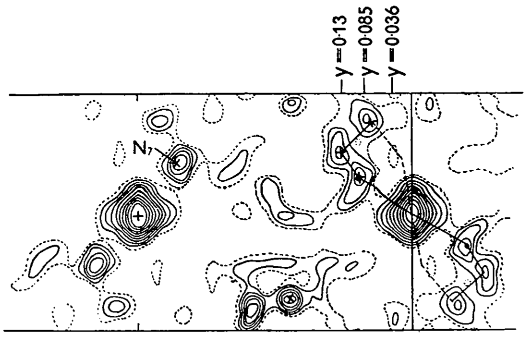

Fig. 5. Parts of the electron-density section at $z = 0$. This section shows an almost complete $Cu(en)_2$ group with the copper at ½, 0, 0. Contours at arbitrary intervals.

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* The present analysis is incapable of deciding whether a carbon or a nitrogen atom of a thiocyanate group is attached to the sulphur atom. However, chemical evidence suggests that the thiocyanate is probably S–C–N, and this has been accepted and is considered in the present discussion.

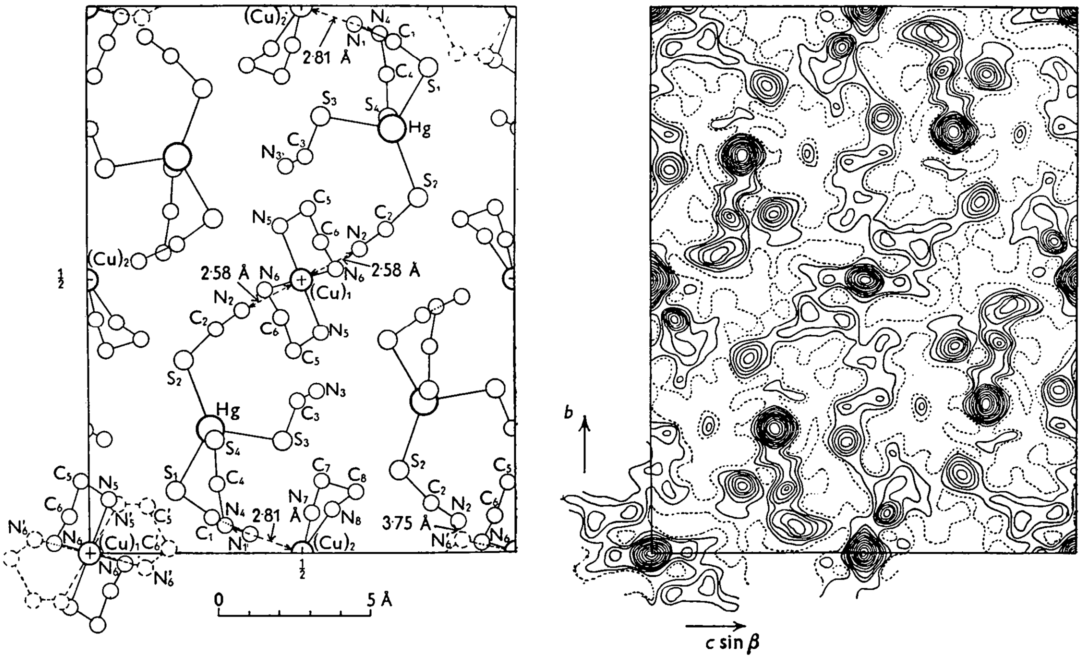

Fig. 6. (*a*) The atomic arrangement in the cell as projected on (100). The alternative orientation of the $(en)_2$ group attached to the copper at the $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ position is omitted to avoid confusion. (*b*) Final electron-density projection on (100), based on the arrangement of atom positions in (*a*). Contour intervals are 20 e.Å^{-2} for the mercury and copper atoms, 4 e.Å^{-2} for the sulphur atoms and 2 e.Å^{-2} for the carbon and nitrogen atoms.

of the corresponding planes by about +0·35 and −0·55 Å respectively.

The bond-lengths and bond-angles in the Cu(en) rings are given in Table 3.

It was found that the $(en)_2$ groups attached to the copper atoms at $\frac{1}{2}$, 0, 0; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ can take up alternative positions, thus indicating two possible stereochemical configurations for these rings. This was suggested by the sections at $x = \frac{1}{2}$ (Fig. 4) and $z = 0$ (Fig. 5), where the $(en)_2$ groups attached to the same copper atom, at $\frac{1}{2}$, 0, 0, are outlined. As the planes $x = \frac{1}{2}$ and $z = 0$ are at right angles, no more than one or two atoms of the same (en) group should appear in these two electron-density sections.

Calculations of the intra-molecular distances between the copper atoms and the nitrogen atoms of the thiocyanate groups gave the values:

$$(Cu)_1\text{–}N_2 = 2{\cdot}58\ \text{Å}, \qquad (Cu)_2\text{–}N_4 = 2{\cdot}81\ \text{Å}\,,$$
$$(Cu)_1\text{–}N_3 = 4{\cdot}06\ \text{Å}, \qquad (Cu)_2\text{–}N_1 = 3{\cdot}60\ \text{Å}\,.$$

These intramolecular distances indicate that the two nitrogens N_2 and N_4 co-ordinate to the copper atoms $(Cu)_1$ and $(Cu)_2$.*

Similar co-ordination from the corresponding nitrogen atoms from the other molecules give a total sixfold co-ordination for each copper atom. The co-ordination directions N_2–$(Cu)_1$–N_2 and N_4–$(Cu)_2$–N_4 are approximately at right angles to the plane containing the copper and the amino-nitrogens.

4. Discussion of the accuracy of the results

The aim of this investigation was to establish the stereochemistry of the $Hg(SCN)_4$ and $Cu(en)_2$ complexes. In the course of the work we experienced many difficulties due to the heavy atoms in the structure. Apart from errors in the observed $|F|$'s, owing to absorption, the diffraction effect of the mercury atom alone could be enough to distort the shapes and heights of the electron-density peaks of the other atoms. Furthermore, no correction was made to allow for the termination of the Fourier series, and it is also possible that some of the signs of the $|F|$'s used in the three-dimensional syntheses are incorrect. It follows, therefore, that of all the interatomic distances and bond angles of Table 3, the most reliable are those between the mercury and the sulphur atoms. The mean Hg–S distance of 2·55 Å is in good agreement with the theoretical value of 2·52 Å, as derived from the atomic radii for a tetrahedrally co-ordinated mercury atom (r = 1·48 Å) and a single-bonded sulphur atom (r = 1·04 Å), and with the experimental values of 2·5 and 2·56 Å observed in the mercury *n*-alkyl mercaptides (Wells, 1937) and chloro-mercury alkyl mercaptides (Johansson, 1939) respectively. Recently, Zhdanov & Sanadze (1952), from X-ray investigation of the $Hg(SCN)_2.K(SCN)$ and $Hg(SCN)_2.NH_4(SCN)$, give Hg–S bonds of 2·51 and 2·45 Å.

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* The notation $(Cu)_1$ and $(Cu)_2$ refers to the copper atoms at $\frac{1}{2}$, 0, 0 or $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ and $\frac{1}{2}$, 0, $\frac{1}{2}$ or $\frac{1}{2}$, $\frac{1}{2}$, 0 respectively.

The bond angles are generally more sensitive to errors in the co-ordinates. However, in spite of the variation of about 20° between two of the S–Hg–S angles, the mean of 109° 16′ is very close to each of the other four S–Hg–S angles. The observed distortion of the HgS_4 tetrahedron is shown in Fig. 7(*a*).

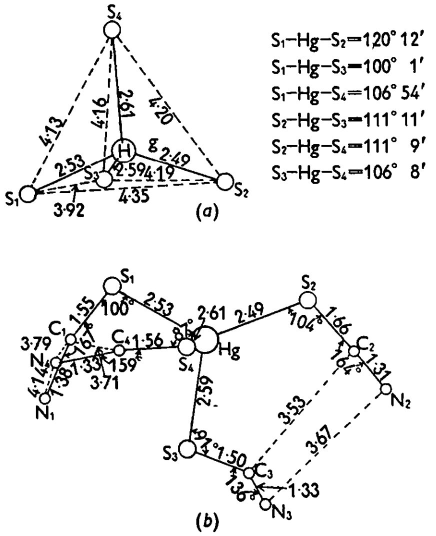

Fig. 7. Interatomic distances, bond lengths and bond angles in (*a*) the HgS_4 tetrahedron, (*b*) the $[Hg(SCN)_4]$ group. All distances in Ångström units.

Although the four sulphur atoms were located with a fair degree of accuracy, this is not the case for the carbon and nitrogen atoms of the (SCN) groups. The following are the weighted mean values for the bond lengths and bond angles of the $Hg(SCN)_4$ group as obtained from this structure analysis:

Hg–S = 2·55 Å   S–Hg–S = 109° 16′
S–C = 1·57 Å   Hg–S–C = 102° 5′
C–N = 1·34 Å   S–C–N = 163° 12′
S–N = 2·90 Å

To our knowledge, no accurately determined crystal analyses of compounds containing the thiocyanate group have so far been reported (Klug, 1933; Zhdanov & Sanadze, 1952).

The mean experimental values of 1·57 and 1·34 Å which we found for the S–C and C–N bond lengths respectively, are, within the limits of error, close to the theoretical values of 1·60 and 1·27 Å as expected for double S–C and C–N bond lengths. There is also good agreement with other experimental values (Table 4).

It is possible, accordingly, that the bond character in the (SCN) group may be the result of resonance between structures:

$$-S-C{\equiv}N,\quad -S^{+}{=}C{=}N^{-}\quad \text{and}\quad -S^{2+}{\equiv}C-N^{2-},$$

in which the second is perhaps predominant.

The interatomic distances and bond angles in $Cu(en)_2$ are generally less accurate than those in the $Hg(SCN)_4$. Here, the Cu–N bond distances should be taken as the more accurate of this group, as there are no errors in the co-ordinates of the copper atoms, and the observed mean Cu–N value of 2·07 Å is close to the expected covalent Cu–N bond of 2·02 Å. The H_2N–Cu–NH_2 angle in all the five-membered rings is less than 90° and would possibly arise as a result of a non-planar ethylenediamine group co-ordinated to the copper atom. Reference can be given here to other saturated five-membered rings for which deviation from planarity was observed. Such examples are: the *d*-ribose ring in cytidine (Furberg, 1950), the thiazolidine ring in penicillin (Crowfoot, Bunn, Rogers-Low & Turner-Jones, 1949), the fructofuranoside (Beevers & Cochran, 1947) and the ring *d* in cholesteryl iodide (Carlisle & Crowfoot, 1945).

5. Conclusions

In carrying out this structure analysis, no preconceived ideas about the stereochemistry of the molecules were employed and the use of the heavy-atom technique has made it possible to arrive at a feasible stereochemical model for the $Hg(SCN)_4$ and $Cu(en)_2$ groups.

The discrepancy factors R for the three projections, using the co-ordinates of all atoms as given in Table 2, were found to be

$$R(0kl) = 0{\cdot}26,\quad R(h0l) = 0{\cdot}26,\quad R(hk0) = 0{\cdot}25\,.$$

These values were further reduced to about 0·16 when empirical f curves for the mercury, copper and sulphur atoms were used.* The f_{Hg} curve was derived from a small number of reflexions for which the mercury atoms were mainly contributing. For the sulphurs, the empirical curve derived from thiophthen (Cox, Gillot & Jeffrey, 1949) was used. From these two f curves the f curve for the copper atom was obtained by interpolation. The f values for the mercury and copper atoms are given in Table 5.

The low values for the discrepancy factors are in no small measure due to the presence of the heavy atoms, but the three-dimensional analyses leave us in no

Table 4. *Observed sulphur–carbon distances*

1·64 Å	in thiourea	Pure double bond	(Wyckoff & Corey, 1932)
1·54 Å	in CS_2	Resonance structure	(Cross & Brockway, 1935)
1·56 Å	in CSO	Resonance structure	
1·56 Å	in CH_3NCS and HCNS	Resonance structure	(Beard & Dailey, 1949, 1950)
1·61 Å	in CH_3SCN	Resonance structure	

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* For the carbon and nitrogen atoms the Robertson $\hat{f}$-curve has been used throughout the analysis.

Table 5. *Experimental atomic scattering factors*

$\sin\theta/\lambda$	Hg	Cu
0·1	78·0	28·5
0·2	71·0	24·0
0·3	58·6	18·0
0·4	40·8	12·5
0·5	38·5	8·4
0·6	22·0	7·5

doubt that the stereochemistry of the $[Hg(SCN)_4][Cu(en)_2]$ structure is essentially what we have described it to be.

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References

BEARD, C. I. & DAILEY, B. P. (1949). *J. Amer. Chem. Soc.* **71**, 929.

BEARD, C. I. & DAILEY, B. P. (1950). *J. Chem. Phys.* **18**, 1437.

BEEVERS, C. A. & COCHRAN, W. (1947). *Proc. Roy. Soc.* A, **190**, 257.

BRAGG, W. L. & WEST, J. (1930). *Phil. Mag.* (7), **10**, 823.

BUERGER, M. J. (1942). *X-ray Crystallography*. New York: Wiley.

CARLISLE, C. H. & CROWFOOT, D. (1945). *Proc. Roy. Soc.* A, **184**, 64.

COX, E. G. (1938). *Rep. Progr. Chem.* **35**, 174.

COX, E. G., GILLOT, R. J. J. H. & JEFFREY, G. A. (1949). *Acta Cryst.* **2**, 356.

CROSS, P. C. & BROCKWAY, L. O. (1935). *J. Chem. Phys.* **3**, 821.

CROWFOOT, D., BUNN, C. W., ROGERS-LOW, B. W. & TURNER-JONES, A. (1949). *The Chemistry of Penicillin*, p. 310. Princeton: University Press.

FURBERG, S. (1950). *Acta Cryst.* **3**, 325.

GOLDSCHMIDT, G. H. & PITT, G. J. (1948). *J. Sci. Instrum.* **25**, 397.

JAMES, R. W. (1948). *Acta Cryst.* **1**, 132.

JEFFERY, J. W. (1947). *Nature, Lond.* **159**, 610.

JOHANSSON, A. (1939). *Ark. Kemi Min. Geol.* A, **13**, Nr. 14.

KLUG, H. P. (1933). *Z. Krystallogr.* **85**, 214.

ROBERTSON, J. M. (1943). *J. Sci. Instrum.* **20**, 175.

ROBERTSON, J. M. & WOODWARD, I. (1940). *J. Chem. Soc.* p. 36.

SCOULOUDI, H. (1951). Ph.D. Thesis, London University.

SCOULOUDI, H. & CARLISLE, C. H. (1950). *Nature, Lond.* **166**, 357.

TUNELL, G. (1939). *Amer. Min.* **24**, 448.

WELLS, A. F. (1937). *Z. Krystallogr.* **96**, 435.

WYCKOFF, R. W. G. & COREY, R. B. (1932). *Z. Krystallogr.* **81**, 386.

ZHDANOV, G. S. & SANADZE, V. V. (1952). *Zh. Fiz. Khim.* **26**, 469.

Acta Cryst. (1953). **6**, 657

Anomalous Lattice Constants of Zinc Oxide

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Samples of zinc oxide examined by X-ray diffraction were found to exhibit (1) axial ratios 1 part in 5000 lower than normal, and (2) significant discrepancies in the lattice spacings determined from different reflexions. The same samples exhibited abnormal electrical conductivities.

With a view to explaining the observations, two hypothetical lattice distortions were considered. It was found that a small change in the nominally 120° angle of the hexagonal cell could be confused with a change in axial ratio, and that changes in the nominally 90° angles together with mutual translations of the atoms could explain the discrepancies in the lattice spacings. Certain samples changed from 'regular' to 'anomalous' behaviour after exposure to the atmosphere, thus suggesting a possible cause for the phenomenon.

Introduction

In a recent report on a series of measurements of the lattice constants of zinc oxide (Rymer & Archard, 1952) it was mentioned that certain samples, excluded from the results given, behaved in an anomalous fashion; for example, their axial ratios fell considerably below the average value, and the lattice spacings deduced from various reflexion planes appeared markedly different, even when the effects of absorption

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