UNIVERSITY OF EDINBURGH

AN X-RAY CRYSTALLOGRAPHIC STUDY OF THE STRUCTURE OF SOME METAL COORDINATION COMPOUNDS.

by

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PART 1

1. INTRODUCTION

Metal ions are common in biological systems and probably function in many cases by complexing with proteins. The study of metal protein interactions has greatly expanded in recent years. The subject was reviewed in 1962 by F.R.N. Gurd [1].

Histidine is a common amino acid in proteins and its imidazole side group has a very high affinity for metal ions. It is therefore not surprising that metal ions are often found to react with histidine residues in proteins. For example in sperm whale metmyoglobin, whose atomic structure is almost completely known [2], a histidyl residue is co-ordinated to the iron atom of the haem group by means of a nitrogen atom of its imidazole ring. The binding of Cu^{++} and Zn^{++} ions to myoglobin in solution [41], principally involves those imidazole groups which are buried within the molecule. It is useful to correlate the ligand properties of these imidazoles with their steric situation which is known from the X-Ray results.

However to predict the properties of an imidazole group in a particular situation is more difficult, and requires an exact knowledge of the properties of the histidyl residue and the neighbouring groups. As F.R.N. Gurd has said [1]: "Only by studying appropriate metal peptides will it be possible to predict the behaviour of each individual potential metal binding site in myoglobin".

In/

In this connection it would be very useful to have precise data on the behaviour of histidine as a ligand. Its properties towards metals in solution are already fairly well known, but these studies do not indicate the exact stereochemistry and conformation of the histidine. Only X-Ray analysis can show the detailed geometry of interaction between histidine and metal atom. This study of nickel histidine is part of a general study of metal-histidine complexes being done in this laboratory. Nickel itself is not an important metal biologically. The interest lies in the comparative study of a series of metal-histidine complexes which might lead to useful conclusions about histidine conformation and metal-oxygen or nitrogen bond lengths.

<u>Work completed on metal-histidine complexes</u>.

(i) Crystallography

Both L and DL complexes of Cd(II), Zn(II), Ni(II) and Co(II) have been investigated at the time of writing. Only the two zinc complexes have been fully reported [3,4]. All the other complexes have been studied in this laboratory (see:- Paper presented to X-Ray Analysis Group Conference, April 1965). All complexes so far determined have two-fold symmetry, and there are some interesting differences between some of the L and DL forms.

(ii) Solution studies.

There have been several independent measurements of metal histidine stability constants [5,6,7] but the most reliable are probably those of Leberman and Rabin [5]. They used potentiometric methods and interpret their results on the basis of two equilibria:-/

equilibria:-

$$M + L^- \overset{K_1}{\rightleftharpoons} ML$$

$$ML + L^- \overset{K_2}{\rightleftharpoons} ML_2$$

	$\text{Log}_{10} K_1$	$\text{Log}_{10} K_2$
Cd (II)	5.65	4.14
Co (II)	6.92	5.52
Zn (II)	6.63	5.67
Ni (II)	8.69	6.83

Their results for Cu^{++} were more complex, the bonding being stronger. The stability constants are all high showing histidine to be a powerful ligand. Among amino-acids only cysteine binds metals more firmly.

Co (II) complexes of histidine have been studied in solution by McDonald and Phillips using N.M.R. [8]. They found that the configuration of the complex varied with pH as might be expected. They could distinguish four complexes, including a tetrahedral $Co(histidine)_2$ complex at high pH.

Other relevant data

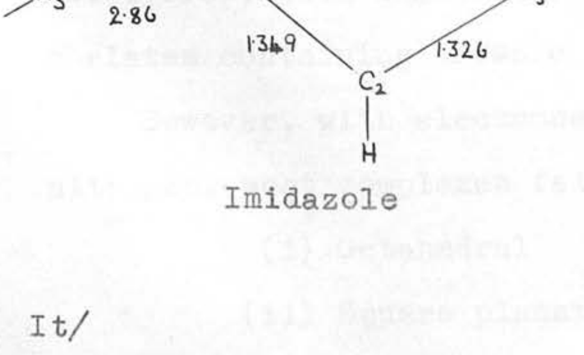
The association of various derivatives of histidine and similar compounds with metals has been investigated [9] in solution e.g. acetyl L-histidine [9], histidyl histidine [9,7], histamine [6], β-(4-imidazolyl) propionic acid [6], anti-histamine [10] and carnosine [11]. Crystallographic work is in progress on Cu(II) glycyl L-histidine [15]. Two independent measurements/

measurements have been made on imidazole-metal stability constants [6,12]. It is useful to compare these constants with the $\log_{10}K_1$ values for histidine.

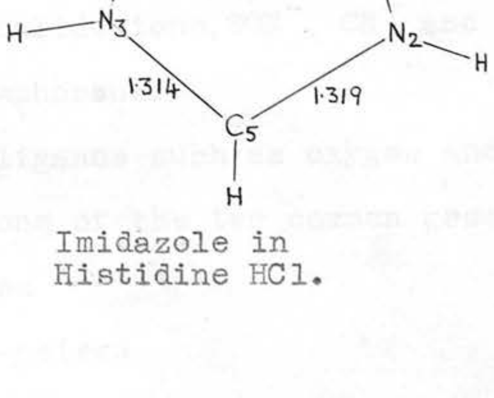
	$\log_{10}K_1$ (histidine) [5]	$\log_{10}K$ (imidazole) [6]
Ni(II)	8.69	3.01
Zn(II)	6.63	2.13

The higher values for histidine are a measure of the strength of binding of the amino and perhaps the carboxyl oxygen, as well as a result of a statistical effect due to chelation. Proof that metals bind to the "pyridine nitrogen" of imidazole, and the total heats of formation of the complexes have been given [12].

Also relevant is the very recent determination of the structure of imidazole by X-rays [13]. The molecule is quite planar, the deviations from the least squares plane being not larger than .004 Å. The hydrogen attached to N_1 is hydrogen bonded to the N_3 of a neighbouring molecule.



Imidazole



Imidazole in Histidine HCl.

It/

It is interesting to compare this structure with the recent refinement of the structure of histidine hydrochloride [14]. In histidine HCl the imidazole ring is protonated at the free nitrogen position, and so small shifts in electron distribution and bond lengths in the ring are to be expected. As may be seen there are some significant differences in bond lengths.

Nickel stereochemistry

Nickel stereochemistry has been reviewed by J.R. Miller in 1962 [16], Nyholm in 1961 [17] and spin-paired complexes of nickel by Harris and Livingstone in 1962 [18].

Two types of spin-free Ni(II) complex are known - octahedral and tetrahedral. Examples of octahedral complexes are very common and well known, but tetrahedral complexes have only become firmly established in the last decade. In the octahedral case electronegative ligands are favoured, whereas tetrahedral complexes mainly occur with halide ions and mixtures of these with triphenyl phosphines.

Similarly with spin-paired Ni(II) complexes, square planar was assumed for a long time to be the only possible configuration. Only recently 5 and 6 co-ordinate spin-paired complexes have been discovered, with ligands including halide ions, SCN^-, CN^- and chelates containing arsenic and phosphorus.

However, with electronegative ligands such as oxygen and nitrogen, most complexes fall into one of the two common groups:-

(i) Octahedral spin-free
(ii) Square planar spin-paired

Ni-O/

Ni-O and Ni-N bond lengths

Table 1 gives data on complexes containing Ni-O and Ni-N bonds whose structures were determined by X-Rays. The observed bond lengths are summarised in Table 2. It is useful to compare these values with the sum of the covalent radii. Pauling [19] gives 1.39Å for the "octahedral covalent radius" of nickel and values of .66Å and .70Å for the covalent radii of oxygen and nitrogen respectively. This gives 2.05Å for the Ni-O bond and 2.09Å for the Ni-N bond, agreeing quite well with the data for octahedral complexes. Tetrahedral and square planar complexes, however, seem to show a significant shortening of about .2Å. This may in part be due to differences in the nature of the ligand atom (all the square planar complexes containing Ni-N bonds have a nitrogen of "imino" character, for example. However the Ni-N(imidazole) distance is normal for the octahedral case). If there is significance in this shortening it would cast doubt on Pauling's conclusion [19] that:- "square dsp^2 radii of atoms have the same values as the corresponding octahedral $d^2 s p^3$ radii".

TABLE 1

COMPLEX	BOND LENGTHS	YEAR	REF.
$Ni(NH_4)_2(SO_4)_2.6H_2O$ containing $[Ni(H_2O)_6]^{++}$ ion. R. Octahedral	$Ni-O(H_2O)$ 2.084(.012) " " 2.04(.012)	1964	20
Tetra kis(aqua)bis(acetato)Ni Regular Octahedral	$Ni-O(H_2O)$ 2.09 Ni-O(carboxyl) 2.12	1953	21
Diaquobis(salicylaldehydato)Ni R. Oct. Coplanar-trans Config. for organic portion	Ni-O(aldehyde) 2.019 $Ni-O(H_2O)$ 2.041(.02) Ni-O(phenolate) 2.023(.02)	1961	22
Bis(salicylaldiminato)Ni Trans planar, centre at Ni	Ni-O(phenolate)1.840(.03) Ni-N(imino) 1.840(.03)	1959	23
Bis(salicylaldoximato)Ni Trans planar, centre at Ni	No accurate bond lengths	1956	24
Bis(N-methylsalicylaldiminato)-Ni. Trans planar	Ni-O(phenolate)1.80(.03) Ni-N(imino)1.90(.02)	1959	25
Bis(N-isopropylsalicylaldiminato)- Ni(II) Distorted tetrahedral	Ni-O(phenolate)1.894(.004) " " " " 1.898(.004) Ni-N(imino)1.990(.005) Ni-N(imino)1.950(.009)	1964	26
Bis(N-nbutylsalicylaldiminato)-Ni. 2 dimensions only.	No accurate bond lengths	1962	27
Diaquobis(acetylacetonato)Ni Tetragonally distorted octahedron	Ni-O(carbonyl)2.018(.01) $Ni-O(H_2O)$2.139(.01)	1964	28
Bis(acetylacetonato)Ni Distorted octahedral. A trimer Pairs of Ni bridged by 3 oxygens	Ni-O(carbonyl)2.00(.04) Ni-O(sharedby other Ni) 2.12(.04)	1961	29
Triethylenediamine Ni nitrate containing $[Ni\ (en)_3]^{++}$ ion. Distorted octahedral.	Ni-N(amino)2.120(.013)	1960	30
Bis(ethylenediamine)bis(isothiocyanato)Ni. $Ni(en)_2(NCS)_2$ Regular Octahedral-trans.	Ni-N(amino)2.10 Ni-N(NCS) 2.15	1963	31
Dinitrobis(NN-dimethylethylenediamine)Ni. Distorted Octahedral	$Ni-O(NO_2)$ 2.11(.008) $Ni-N(NMe_2)$ 2.219(.012) Ni-N(amino) 2.089(.009)	1964	32

TABLE 1. (continued)

COMPLEX	BOND LENGTHS	YEAR	REF.
Dinitrobis(ethylenediamine)Ni perchlorate. $[Ni(en)_2(NO_2)_2]^{++}$ ion Chain structure. R.Octahedral. Ni atoms linked by O of NO_2	Ni-O(NO_2) 2.58(.04) Ni-N(amino)2.17(.04) " " 2.13(.04)	1962	33
Bis(dimethylglyoximato)Ni. Trans planar.	Ni-N(imino) 1.87(.02) " " 1.90(.01)	1953	34
Bis(methyl ethyl glyoximato)Ni Trans planar.	Ni-N(imino) 1.83(.02) " " 1.88(.02)	1960	35
Bis(glycino) Ni dihydrate Distorted octahedral.	No accurate bond lengths	1945	36
Bis(β-alanine)Ni dihydrate Very slightly distorted octahedral.	Ni-O(carboxyl)2.14(.02) Ni-O(water) 2.17(.02) Ni-N(amino) 2.10(.03)	1964	37
Bis(DL-histidino) Ni - monohydrate. Regular octahedral.	Ni-O(carboxyl)2.109(.010) Ni-N(amino) 2.102(.01) Ni-N(imidazole)2.094(.007)	1965	This thesis
Ni triammine dithiocyanate Regular octahedral.	Ni-N(amino) 2.024(.016)	1956	38
Bis(thiosemicarbazidato)Ni Trans planar.	Ni-N(imino) 1.91 (.01)	1962	39
Ni etioporphyrin 4-coordinate but not planar.	Ni-N(imino) 1.96 (.01)	1963	40

TABLE 2

Ni - O and Ni - N bond distances

O (water)

2.08	(.01)	R. Oct.	20
2.04	(.01)	"	20
2.04	(.02)	"	22
2.09		"	21
2.14	(.01)	D. Oct.	28
2.17	(.02)	"	37

O (carboxyl)

2.12		R. Oct.	21
2.11	(.01)	"	This thesis
2.14	(.02)	D. Oct.	37

O (carbonyl)

2.02	(.02)	R. Oct.	22
2.00	(.04)	D. Oct.	29
2.02	(.01)	"	28

O (phenolate)

1.89	(.004)	D. Tetr.	26
1.90	(.004)	"	26
2.02	(.02)	R. Oct.	22
1.84	(.03)	T.Planar	23
1.80	(.03)	"	25

O (NO_2)

2.58	(.04)	R. Oct.	33
2.11	(.01)	D. Oct.	32

O (other)

2.12 (.04) O shared by other Ni atom. D.Oct. 29

N (amino)

2.02	(.02)	R. Oct.	38
2.10		"	31
2.17	(.04)	"	33
2.13	(.04)	"	33
2.10	(.01)	"	This thesis
2.10	(.03)	D. Oct.	37
2.09	(.01)	"	32
2.12	(.01)	"	30

N (imino)

1.84	(.03)	T. Planar	23
1.90	(.02)	"	25
1.83	(.02)	"	35
1.88	(.02)	"	35
1.87	(.02)	"	34
1.90	(.01)	"	34
1.91	(.01)	"	39
1.99	(.005)	D. Tetr.	26
1.95	(.009)	"	26
1.96	(.01)	Non-Planar	40

N (other)

2.09 (.01) Imidazole R. Oct. - This thesis.

2.15 -NCS R. Oct. 31

2.22 (.01) $-NMe_2$ -D.Oct. 32

Notes
R. Oct. = Regular Octahedral
D. Oct. = Distorted Octahedral
D. Tetr.= Distorted Tetrahedral
T.Planar= Trans Planar

2. DETERMINATION OF THE STRUCTURE OF DL BIS-(HISTIDINO) Ni(II) MONOHYDRATE.

(a) Preparation of complexes of Ni(II) with DL Histidine.

Two different crystalline complexes of Ni(II) with DL histidine were prepared as follows:-
Ni CO_3 was added to a solution of pure DL histidine. There was no reaction in the cold, but on boiling there was a vigorous reaction, evolution of CO_2 and a blue-purple colour appeared. Slow cooling and evaporation gave a background of small purple crystals, together with several larger deep blue crystals. Use of different proportions of $NiCO_3$: histidine did not alter the crystals obtained. Better quality crystals of both types were prepared by recrystallisation from boiling water, with slow cooling to room temperature and evaporation.

The purple crystals (A) were small with good faces, sharp reflections and were stable in air at room temperature. (See Fig 1 and page 9). The deep blue crystals (B) were larger (> .2mm), had a cubic shape, but did not have such good faces, and decomposed after a short exposure to air. X-Ray powder photographs were taken of crystals A, B and pure DL histidine. All three photographs were different from one another.

Crystals B

The density was determined by flotation in a mixture of carbon tetrachloride and methyl iodide $\rho_{obs} = 1.667$ g.cm^{-3}. The unit cell volume was measured by taking photographs about an/

an axis, parallel to one of the prominent crystal zones, whose translation was 15.05 (± .1)Å. The crystal was mounted in a sealed "Pantak"* tube. No symmetry was observed on the oscillation or zero layer Weissenberg photographs. The cell volume, V_c, was 787 (± 15)$Å^3$. V_c together with ρ_{obs} gives a cell molecular weight of 790 (± 15). This is very close to the sum (= 788) of the molecular weights of 3 molecules of water and two molecules of Ni(histidine)$_2$. The density calculated from V_c and this cell contents is 1.663 $g.cm^{-3}$. It should be noted that the real unit cell volume may be a multiple of V_c quoted above, since systematic absences may have been present.

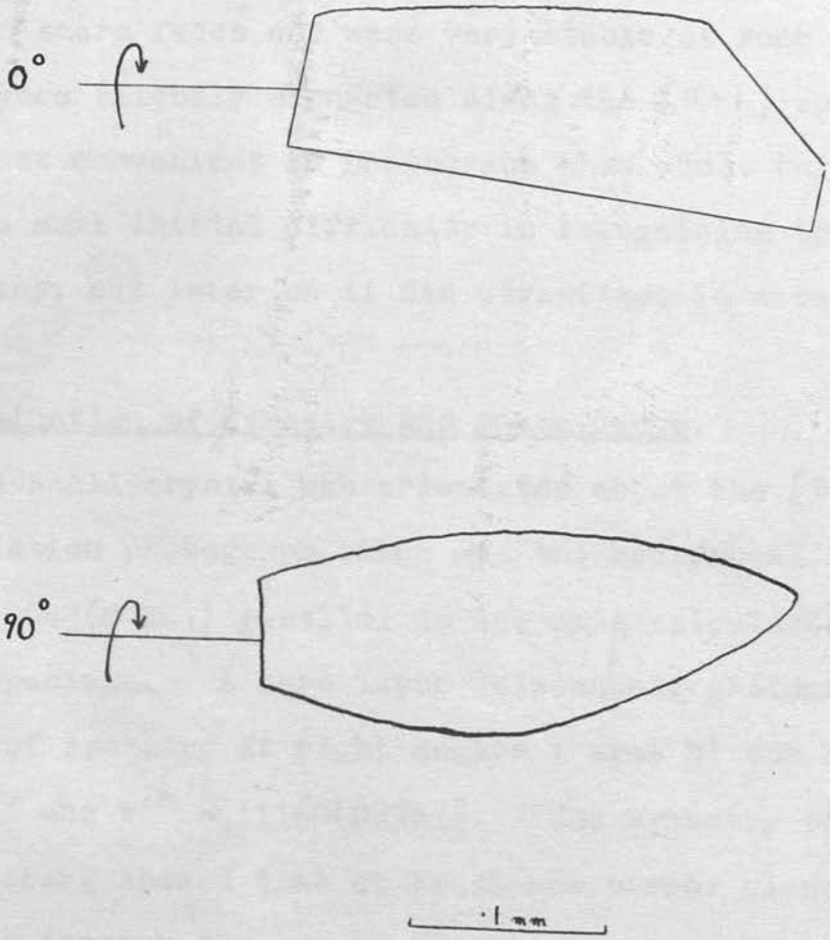
Investigation of these crystals was stopped at this point, since their instability made them unsuitable for accurate work. It was concluded that there is a 3:2 ratio of water:Ni (histidine)$_2$ in crystals B.

Crystals A

The great stability of these crystals and the beauty of their crystalline form, made them suitable for a full structural investigation. The determination of symmetry and space group showed the problem of structure analysis to be greatly simplified. The rest of this section therefore describes the full structure analysis of crystals A, which were proved to be Ni(histidine)$_2$.H_2O or more formally, DL bis-(histidino) Ni(II) monohydrate.

* "Pantak" tubes are very thin walled glass capillary tubes

Fig. 1



Projections of Crystal of Ni(histidine)$_2$. H_2O

[01$\bar{1}$] Rotation Axis in Plane of Paper.

(b) Preliminary work on Ni(Histidine)$_2$.H$_2$O (Crystals A).

Small purple crystals A were recrystallised from boiling water. They were rather irregular in shape (see Fig. 1), but showed sharp faces and were very stable at room temperature. They were slightly elongated along the $[01\bar{1}]$ zone axis, and it was most convenient to photograph them about this axis. This led to some initial difficulty in recognising their orthrhombic symmetry, but later on it had advantages in data collection.

Determination of Symmetry and Space Group.

A small crystal was orientated about the $[01\bar{1}]$ axis and an oscillation photograph taken and the reciprocal lattice spacing $d^* = \cdot 2043$(CuKα_1) parallel to the axis calculated from the layer line spacings. A zero layer Weissenberg photograph showed two lines of symmetry at right angles : axes h' and k' with a'^* $= \cdot 1013$ and $b'^* = \cdot 1160$(CuKα_1). The symmetry of the zero layer Weissenberg showed that at least one mirror plane was present passing through the origin of reciprocal space. The 1st, 2nd and 3rd layer equi-inclination photographs showed only one line of symmetry parallel to k'. The mirror plane was therefore normal to the h' axis, and the crystal was therefore monoclinic or had higher symmetry.

Assuming it to be monoclinic, a' was the unique axis and the films were indexed accordingly. The systematic absences found did not fit in with any monoclinic space group. The crystal/

crystal therefore had higher symmetry.

A plot was made of the reciprocal lattice normal to the h' axis and only the observed reflections marked on it (see Fig. 2). At once a face centred pattern emerged. It was possible to choose a new axis, named k, and an axis 1 at right angles approximately. The axis h' was renamed h. There were two possibilities of choosing k and 1 as indicated on Fig. 2. If the crystal was orthorhombic the hkO and hO1 planes would be mirror planes. The films were next indexed according to the two possible orientations of k and 1, and the intensities of reflections on layers 0 to 3 related by the mirror planes compared roughly. One orientation gave good agreement; the other no agreement at all. The k and 1 axes were chosen accordingly as shown in Fig. 2. This in itself was a strong indication of orthorhombic symmetry. The final proof was in the observed conditions of reflection:-

hkl	only for	k + 1 = 2n
Okl	only for	1 = 2n, k = 2n
hol	only for	h = 2n, 1 = 2n
hko	only for	k = 2n
hoo	only for	h = 2n
oko	only for	k = 2n
ool	only for	1 = 2n

These conditions indicated A face centring, a glide plane normal to a, and a glide plane normal to b with translation a/2. The crystal/

crystal was therefore orthrhombic with space group no. 41 (Aba2) or No. 64.

Henceforth when axes are mentioned they will refer to the indexing system consistent with space group Aba2.

Accurate Unit Cell Measurement.

A crystal was mounted about the b-axis and a zero layer Weissenberg photograph taken with Cu Kα radiation. It was calibrated by means of a fine copper wire which was photographed at both top and bottom of the Weissenberg film. The copper lines were indexed and their θ values calculated. $a = 3.61504$Å for copper (face centred cubic) was used. The distance between the corresponding lines on either side of the film was measured with a travelling microscope, and the distance : angle conversion factor was calculated for each line and plotted against $\sin^2\theta$. This was done for both top and bottom of the film and extrapolation to $\sin^2\theta = 1$ gave the same value for the conversion factor, namely .05010 cm/degree. This should eliminate errors due to absorption, eccentricity, divergence of the beam and film shrinkage.

A value of a^* was determined by measuring the distances across the film between corresponding h o o reflections. The conversion factor was used to calculate a^* for each reflection (α_1 and α_2 spots where possible) and these values were plotted against $\sin^2\theta$ and extrapolated to $\sin^2\theta = 1$. This was done for 10.0.0, 12.0.0, 14.0.0, and 16.0.0. Lack of any reflections above/

above $\sin^2\theta = .67$ limited the accuracy of the result:-

$a^* = .10151$ M.P.E. (Maximum possible error) =

$\pm .00010$ (Cu Kα_1).

Unfortunately an accurate value of c^* could not be obtained from the photograph since there were very few ool reflections.

A value of b^* was obtained from a precession photograph of the hko plane taken with Mo Kα radiation. The film was calibrated from the value of a^* determined previously. Distances across the film between corresponding spots were measured as before. In this case the variation of $\sin\theta$ with distance is linear, and so an averaged $\sin\theta$: distance conversion factor was calculated from the hoo reflections : .04172/cm. Values of $\sin\theta$ for the oko reflections were obtained using this factor, and values of b^* calculated.

b^*(average) = .05435 M.P.E. = $\pm$ .00010 (MoKα_1)

or b^*(average) = .11805 M.P.E. = $\pm$ .00021 (Cu Kα_1).

A value of c^* was obtained by measuring the zero layer Weissenberg of a crystal set up about the [$01\bar{1}$] axis (CuKα radiation). It was calibrated by measuring the hoo reflections. A distance : angle conversion factor was obtained in the manner described for the copper wire lines. Reflections of the type okk were then measured and their $\sin\theta$ values calculated using the conversion factor. Next, using the value $b^* = .11805$, c^* values were calculated for each reflection, plotted against $\sin^2\theta$ and extrapolated to $\sin^2\theta = 1$.

c^*/

c^{*} = .1996 M.P.E. = $\pm$ .0005 (Cu Kα_1)

It was unfortunate that by this method the values of b^{*} and c^{*} depend on the value of a^{*} which was used for calibration. The final unit cell dimensions are given in Table 3, and they were used throughout the rest of the work.

Density

The density of crystals A was determined by flotation in a mixture of carbon tetrachloride and methyl iodide. Freshly prepared crystals were used.

$$\rho_{obs} = 1.671\ (\pm\ .004)\ g.cm^{-3}.$$

Effect of temperature

A small sample (.02 g) of crystals A was heated at 150°C to constant weight (20 hours). The percentage loss in weight was 1.13%. No change was observed in the crystals and they still had good faces and sharp reflections. They appeared to be very stable at this temperature.

Conclusions from Space group, cell volume and density.

The measured cell volume, V_c was 1528.6 $Å^3$. This together with the observed density gives a total "cell molecular weight" of 1538.5.

Assuming a complex of the type Ni(histidine)$_2$ with MW = 367.05, the total weight of 4 molecules of this complex and 4 molecules of water would be 1540.3. This agrees well with the observed/

observed "cell molecular weight" of 1538.5. Further work therefore proceeded on the assumption that there are 4 molecules of Ni(histidine)$_2$ and 4 of water in the unit cell.

On this basis the density, calculated from the contents of the cell and the cell volume, is: $\rho_{calc} = 1.673$ g. cm^{-3}. This value agrees with ρ_{obs} within experimental error. The two possible space groups are:-

(i) Aba2. (No.41)

This space group has eight equivalent positions, and four special positions on the two-fold axes. It is non-centrosymmetric. To fit the cell contents to the space group the four Ni atoms and the four oxygens of the water molecules would have to lie on the two-fold axes, while the histidine atoms would be in general positions. Any Ni(histidine)$_2$ complex would therefore have two-fold symmetry.

(ii) No. 64

This space group has sixteen general equivalent positions, and a series of eight-fold and four-fold special positions. Since there are eight histidine units in the cell, each histidine atom would have to occupy a special position. This is obviously impossible.

The space group is therefore Aba2.

Linear absorption coefficient

The linear absorption coefficient for Cu Kα radiation was calculated:

$$\mu = 23.5\ \text{cm}^{-1}$$

The formula: $\mu = \rho \sum p\, \mu_m$ was used where:

$\rho = 1.673\ \text{g cm}^{-3}$

μ_m = Mass absorption coefficient [42]

p = proportion by weight of element present.

(c) Data Collection

3-Dimensional data was collected from the crystal shown in Fig. 1. The crystal was mounted with secotine on the end of a very fine glass fibre on a goniometer head. The camera was a Unicam equi-inclination Weissenberg camera of diameter 57.3 mm. A stabilised Philips X-Ray set with sealed copper target tube was used and was normally run at 40 KV and 20 m A, with a nickel filter. The collimator and beam-stop were of brass.

Film Technique

The multiple film method was employed with a pack of four Ilford Industrial G films for long exposures of about 50 hours. It was usually necessary to take another short exposure with a single film in order to get measurable intensities for the strongest reflections. Intensities from a pack of films were put on the scale of the top film by calculation of the inter-film scale factors. Usually about twenty or more reflections common to two films were measured on a reliable part of the intensity scale. The ratio of the intensities were then averaged. Scale factors for neighbouring G films varied from 2.9 to 3.3. Due to the dangers of differences in film quality, developing etc., film factors were calculated independently for each film.

Strategy

The crystal was first accurately adjusted to the [0 1 $\bar{1}$] zone axis. The oblique axis was a great advantage for data collecting, because/

because it enabled about 94% of the unique reflections to be measured from a single crystal setting. This may be seen by reference to Fig. 2. In the orthorhombic system $\frac{1}{8}$th. of the reciprocal lattice is unique, for example the h k l sector for h,k,l ⩾ 0; i.e. the red and green areas for h ⩾ 0 in the figure. The various layers normal to the $[01\bar{1}]$ axis are shown as vertical lines. It was possible to take photographs up to layer 6 which had an equi-inclination angle $\mu = 37.7°$. This covered the green area of the reciprocal lattice for all values of h.

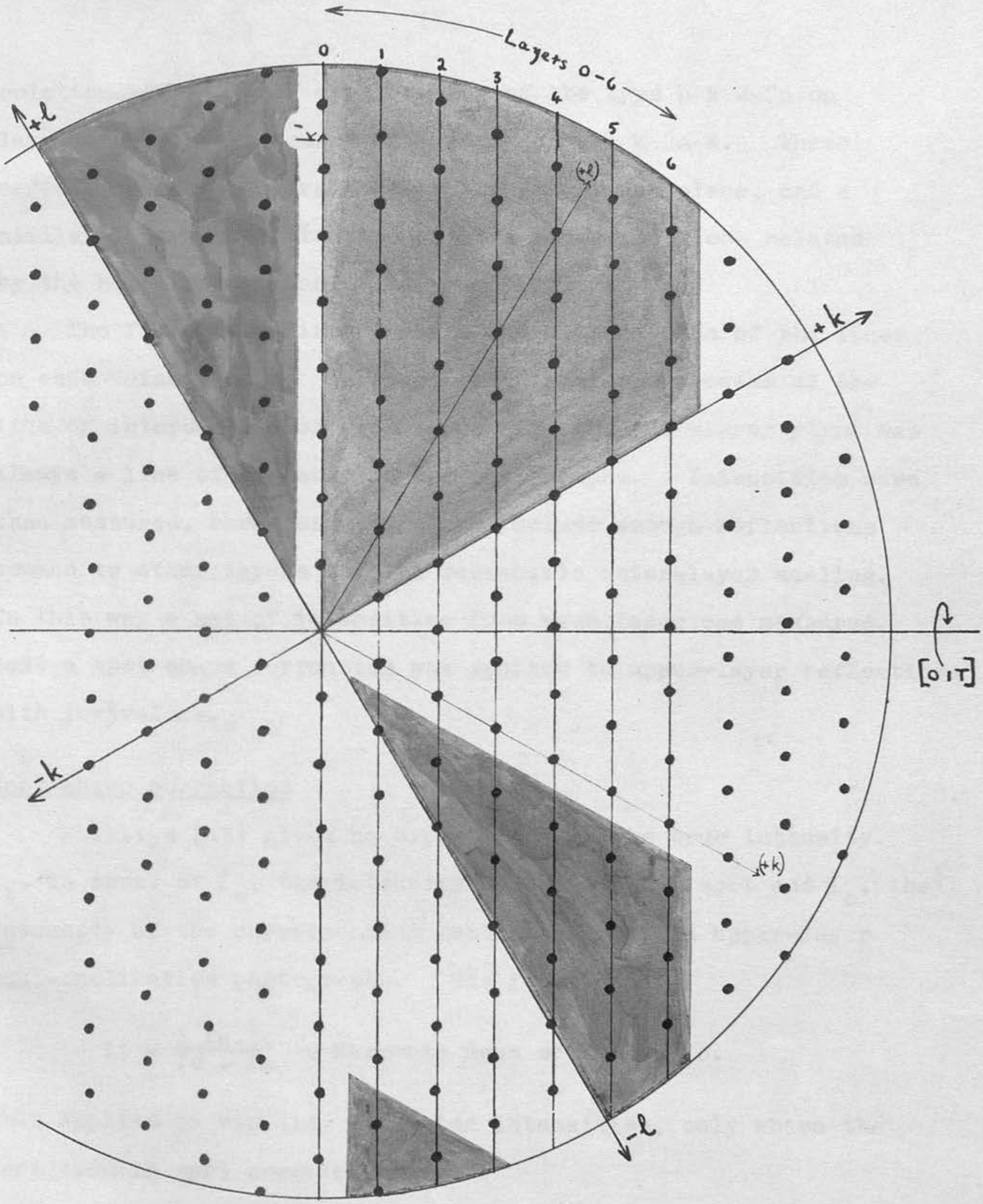
The red region is related by the hko mirror plane to the blue area which could be measured on the photographs. The only reflections remaining unrecorded were those on the seventh and eighth layers, and these numbered only thirty-three. Therefore out of a total of over nine hundred unique reflections only thirty-three could not be recorded. There was also the further advantage that "automatic inter-layer scaling" was possible without the necessity of taking any more photographs.

The reflections occurring on the layers were of the following types:-

Zero layer	h k k
1st layer	h k k-2
2nd layer	h k k-4
n th layer	h k k-2n.

Now a reflection of the type hkk on the zero layer could also be measured on layer k as h k $\bar{k}$. Reflections on layer 1 of the type h k k-2 could be measured on layer k-1 as h k 2-k. The general relationship/

Fig 2



Okl Reciprocal Lattice

The other (incorrect) set of axes are marked: (+k), (+l) (see Page 10) relationship was that a reflection of the type h k k-2n on layer n could be measured on layer k-n as h k 2n-k. These reflections were all related by the hko mirror plane, and a similar general relationship existed for reflections related by the hol mirror plane.

The films were first indexed and a trace made of the lines on each Weissenberg. This was quite a simple process as the line of intersection of each layer with the okl mirror plane was always a line of symmetry on the photographs. Intensities were then measured, care being taken to include enough reflections common to other layers to give reasonable inter-layer scaling. In this way a set of intensities from each layer was measured. Next a spot shape correction was applied to upper-layer reflections with low ξ values.

Spot shape correction

Phillips [43] gives an expression for the true intensity, I_t, in terms of I_e, the intensity of an extended spot and I_c, the intensity of the corresponding contracted spot on upper-layer equi-inclination photographs. His formula is:-

$$It = \frac{2\ Ie.Ic}{Ie + Ic} = \text{Harmonic mean of Ie and Ic.}$$

This applies to visually estimated intensities, only where the variation in spot area is small.

However badly distorted spots on upper layers with low ξ values never had to be measured, as may be seen by reference to Fig. 2. They/

They were always measured in some other region of reciprocal space at higher ξ values. Phillips formula was therefore taken to apply with reasonable accuracy to all cases. Ie and Ic values were estimated for a selection of spots, (usually twenty or more), at various ξ values on layers 1 to 6. The ratio $\frac{It}{Ie} = \frac{Ic}{\frac{1}{2}(Ie + Ic)}$ was calculated for each pair of spots and plotted against ξ. The curve was used to correct extended spots which were measured in preference to contracted spots where possible. Sometimes contracted spots had to be measured, and in these cases the correction factor $\frac{It}{Ic} = 2 - \frac{It}{Ie}$ was used.

Absorption correction

At this stage a correction for absorption was considered. The crystal used (see Fig. 1) was very roughly a cylinder of diameter .1 mm. With $\mu = 23.5$ cm^{-1} this gives a value $\mu R = .12$. W.L. Bond [44] gives values of A^*, the absorption correction factor, for cylinders at successive values of θ (Bragg angle). At $\mu R = .12$ the maximum variation of A^* (between $\theta = 0°$ and $\theta = 90°$) is only about 1%. A larger error is probably caused by changes in the effective value of μR due to the irregular shape of the crystal. But assuming a maximum variation of 10% in μR, the corresponding variation in A^* is only 2%. This means that a maximum variation of 3% in A^* is likely. A similar variation would be expected for upper layer photographs. 3% Is very much smaller than the expected random errors in intensity measurements ($\sim$10%). No absorption/

absorption correction was therefore attempted.

Intensity processing

After spot shape correction, the intensities on each layer were LP corrected using a program (Harding 8/2) written in EMA for Atlas. Intensities on different layers could now be compared directly, and the final problem was to derive reliable inter-layer scaling factors.

First every possible pair of layers was taken and the common reflections tabulated. An averaged ratio of intensities was taken as the scale factor, leaving out reflections thought to be unreliable for one reason or another. An agreement or R factor ($R = \frac{\Sigma \Delta}{\Sigma I}$) was calculated, and the following two tables show the results:-

Interlayer scale factor

n =	1	2	3	4	5	6
0/n	·917	·848	1·843	·838	-	-
1/n		·937	1·950	·942	1·114	-
2/n			1·882	1·279	1·218	-
3/n				·513	·728	-
4/n					·761	·382
5/n						·901

Corresponding R factors (%)/

Corresponding R factors (%)

n =	1	2	3	4	5	6
0	5.4	5.9	23.4	24.4	-	-
1		11.2	9.3	18.7	11.4	
2			7.9	28.4	5.2	-
3				15.1	25.1	-
4					5.8	17.3
5						22.9

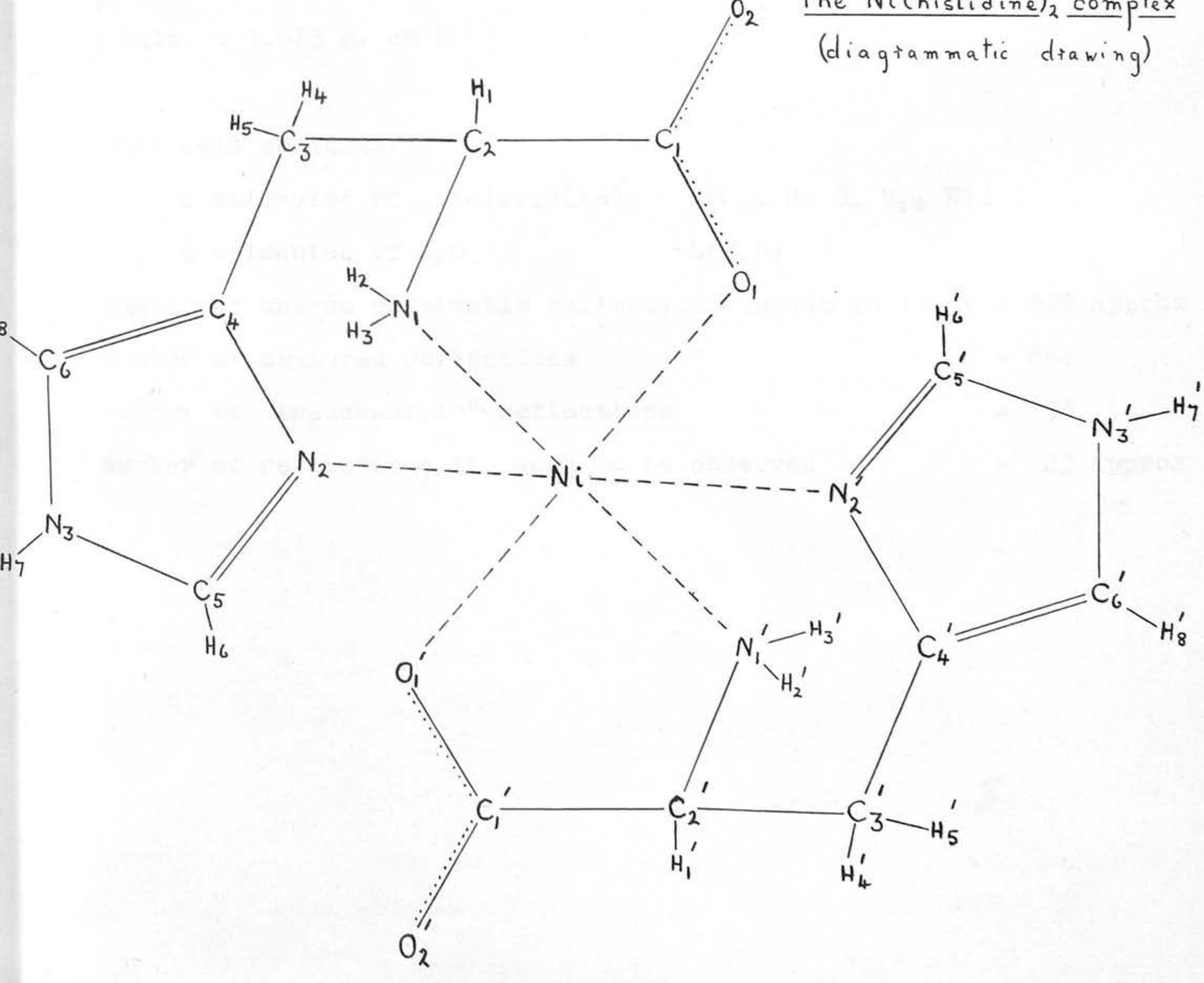
The R factors show a wide variation, some being quite good (5.2 - 11.2%) others (> 20%) being rather poor. This was attributed mostly to differences in spot shape between the two layers. Also some R. factors were probably high due to the small number of common reflections available.

Scale factors were derived for each layer, taking the factor for layer 1 as 1.000. This could have been tackled by a formal process of least-squares refinement with a weighting scheme depending on the R factors. But in view of the large variation in R factors and reliability of the scale factors, this did not seem worth while. Instead the most reliable values were judged, and a rough process of averaging gave the final inter-layer scale factors:-

Layer	Scale factor
0	1.091
1	1.000
2	.931
3	1.752
4	.918
5	.917
6	.826

Each layer was scaled with these factors, and a list of unique intensities drawn up. Where an intensity was measured on two or more different layers, the reliability of each value was scrutinised and only the most reliable one taken. If the values were equally reliable, then they were averaged.

A process of sorting then gave the final list of intensities which were now proportional to F^2. They were punched out on tape, reflections too weak to be observed being omitted from the list.



The Ni(histidine)$_2$ complex
(diagrammatic drawing)

TABLE 3

SUMMARY OF DATA FOR NI(HISTIDINE)$_2$ H$_2$O.

Orthorhombic.

a = 15.18 (± .015) Å a^*(Cu Kα_1) = .1015 M.P.E. = .10%

b = 13.05 (± .023) Å b^*(") = .1181 M.P.E. = .18%

c = 7.72 (± .019) Å c^*(") = .1996 M.P.E. = .25%

Vc = 1529 Å^3

Space Group Aba2 (No. 41)

Linear absorption co-efficient, μ = 23.5 cm^{-1} (Cu Kα)

ρ obs = 1.671 g.cm^{-3}

ρ calc. = 1.673 g. cm^{-3}

Unit cell contents:

4 molecules of Ni(histidine)$_2$ 4(C_{12} N_6 O_4 H_{16} Ni)

4 molecules of H_2O 4(H_2O)

Number of unique observable reflections inside Cu limit = 920 approx

Number of measured reflections = 864

Number of "inaccessible" reflections = 33

Number of reflections too weak to be observed = 23 approx

(d) The problem of solving the structure

General

In a non-centrosymmetric crystal the heavy-atom method depends on the phases calculated from the heavy atom, α_H, resembling the true phases α. The distribution of errors in the phases is a function of r where $r = \left(\frac{\sum f_H^2}{\sum f_L^2} \right)^{\frac{1}{2}}$ [45]. r depends on the ratio of the sums of the squares of the atomic numbers of the heavy atoms to those of the light atoms. The larger the value of r, the smaller the errors in phases. Too large a value of r, however, often results in the light atoms being "swamped" by the heavy ones, and their co-ordinates become inaccurate. In extreme cases the light atoms may even disappear completely into the background electron density. Too small a value of r, on the other hand, while it leads to accurate light atom co-ordinates, may mean some difficulty in solving the structure, since the errors in the phases will be quite large. In practice a compromise must be reached, and the most useful value of r is about 1.0.

Now in Ni(histidine)$_2$.H$_2$O, $f^2_{Ni} = 784$, $f_L^2 = 1064$ and $r = \cdot 86$. This is therefore a fairly favourable case for application of the heavy-atom method.

With space group Aba2 and 4 molecules of Ni(histidine)$_2$ in the unit cell, the problem of solving the structure was relatively simple. The Ni atoms must lie on the two fold axes, and the molecule of Ni(histidine)$_2$ must possess exact two-fold symmetry, in the crystalline state at least. Now in Aba2, being non-/

non-centrosymmetric, the origin can be placed anywhere on the two fold axes, and it is most convenient to take it at the Ni atom.

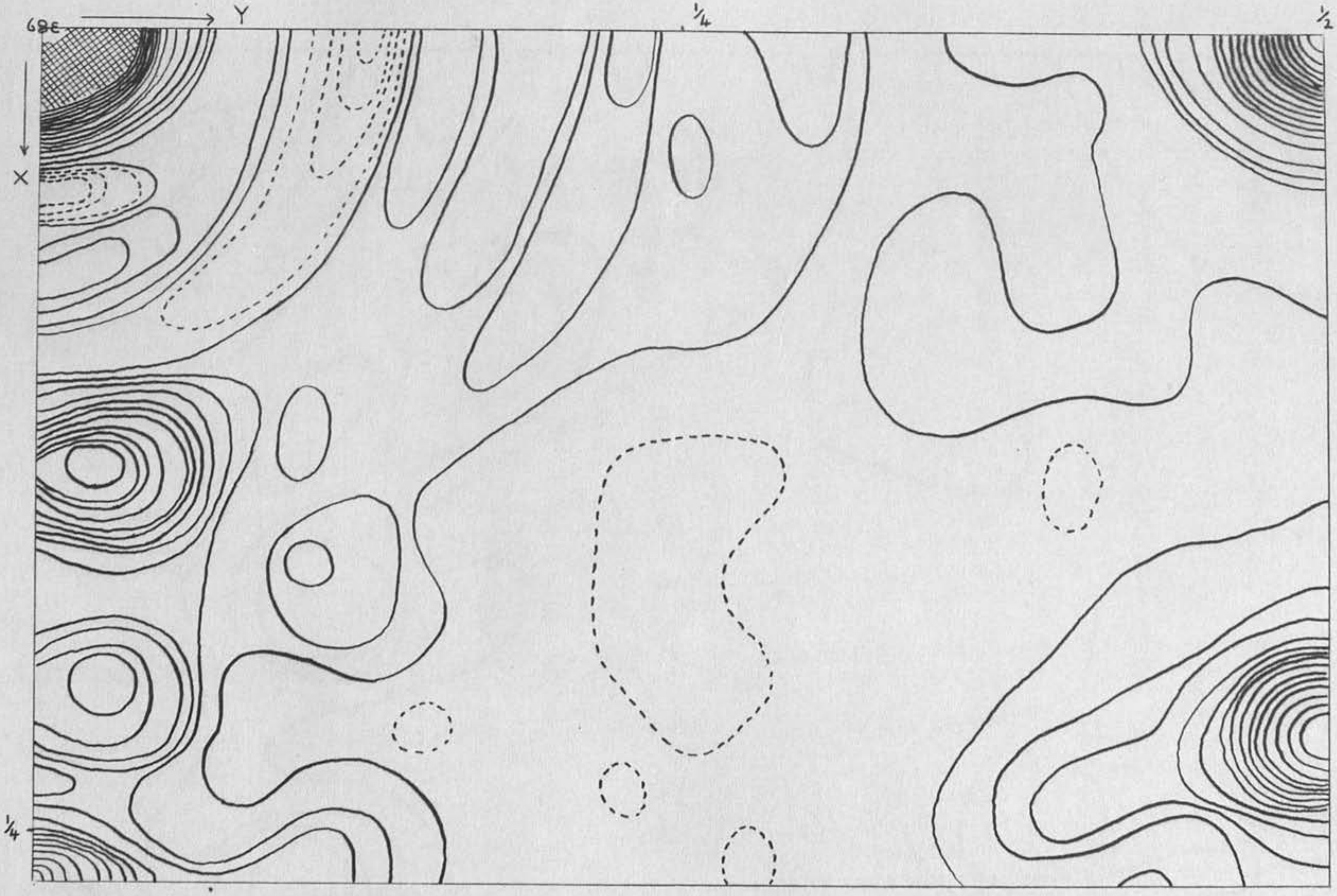
Knowing the exact position of the Ni atom, Fourier methods were used to find the light atoms. The only difficulty in the solution of the structure was encountered at this stage, and it was due to the special position of the Ni atom which gave pseudosymmetry in the Fourier phased on it. However it was possible to break this false symmetry and derive the correct structure. This process and the refinement of the structure is summarised in Table 4.

The single water molecule present in the crystal, must of course lie on the two-fold axis, there being only four in the unit cell. Now the distance between neighbouring Ni atoms along this axis is 7.7 Å. Although no z/c parameter could be assigned to the oxygen at this stage, it was noted that there is enough room to accommodate the water molecule without the necessity of its being bound to the Ni as a ligand.

Patterson Synthesis

A 3-dimensional Patterson synthesis was first considered, but rejected after comparing its properties with those of the Fourier phased on the Ni at 0,0,0. The Patterson of Aba2 has the symmetry of space group Ammm[46], while the Fourier phased on Ni has the symmetry of Fmmm. Thus the Patterson and Fourier would be expected to resemble one another quite closely. In the Patterson there would be an image of the structure in the Ni atom, together with/

Fig 3 (i)



$Z = 0/24$

Ist 3-D Fourier

Fig 3 (i) - (vii)

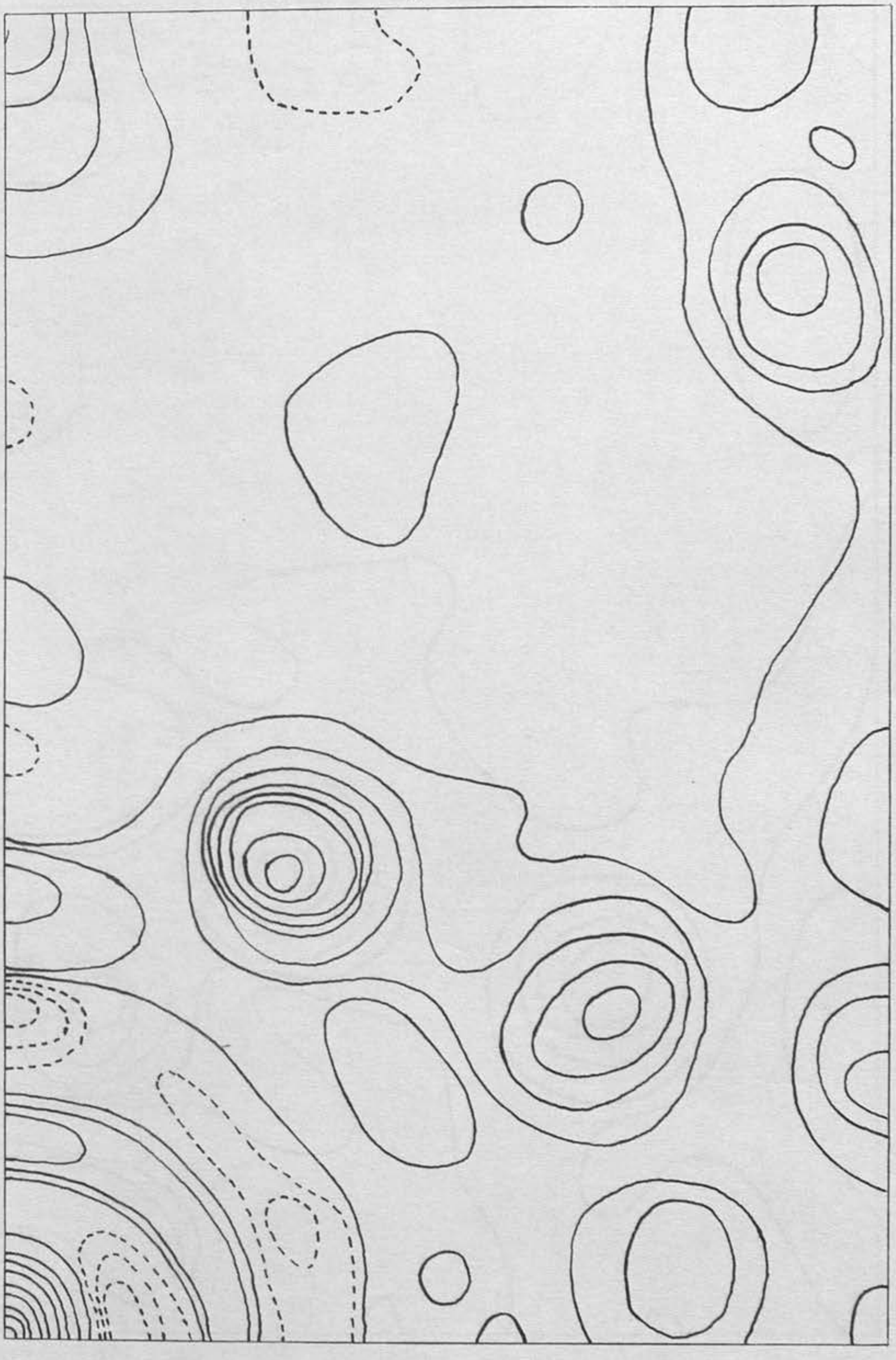
Contours at intervals of $\frac{1}{2}\ e\ \mathrm{\mathring{A}}^{-3}$

Zero and negative contours : ----------

Fig 3 (ii)

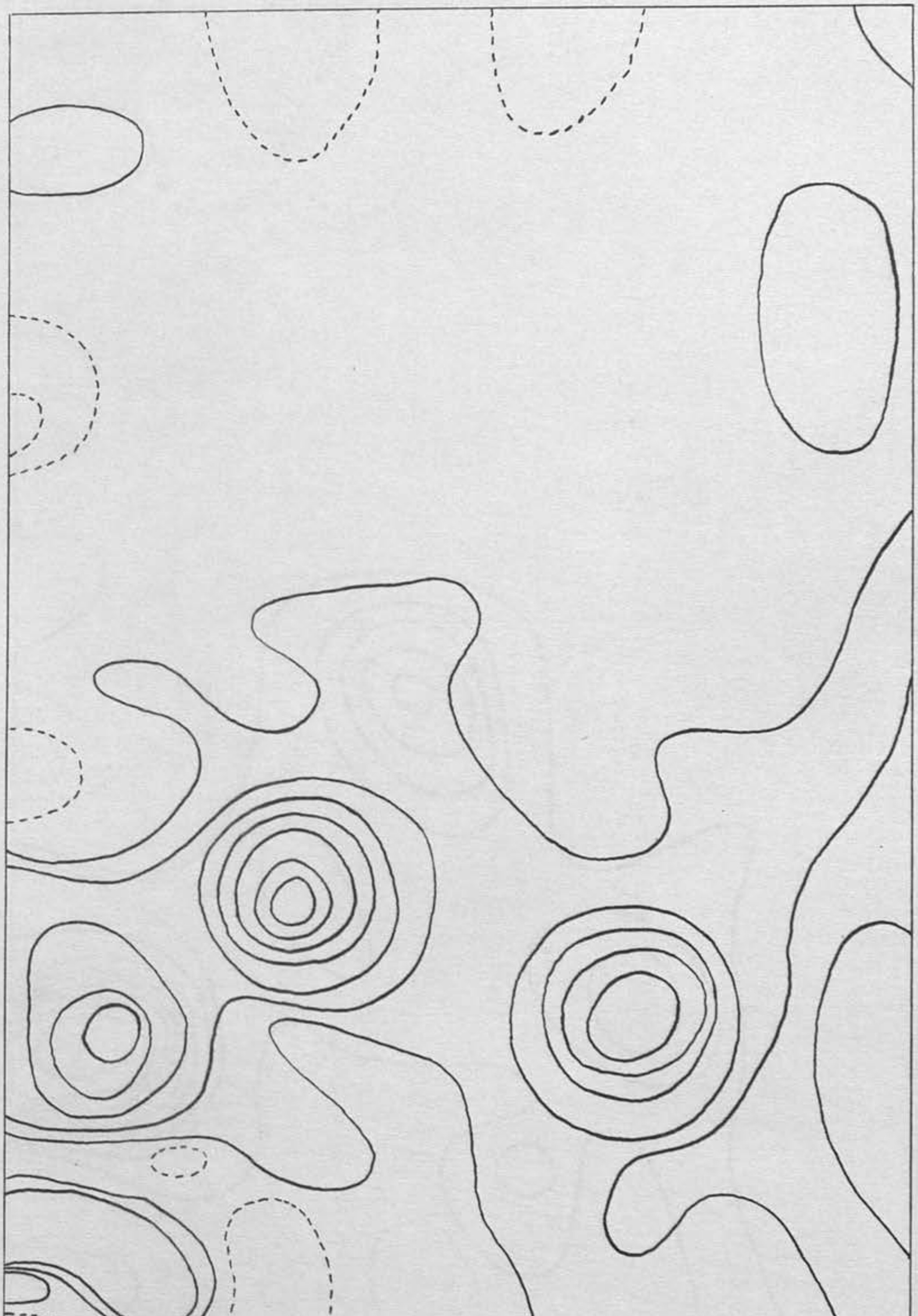
Z = 1/24

Fig 3 (iii)



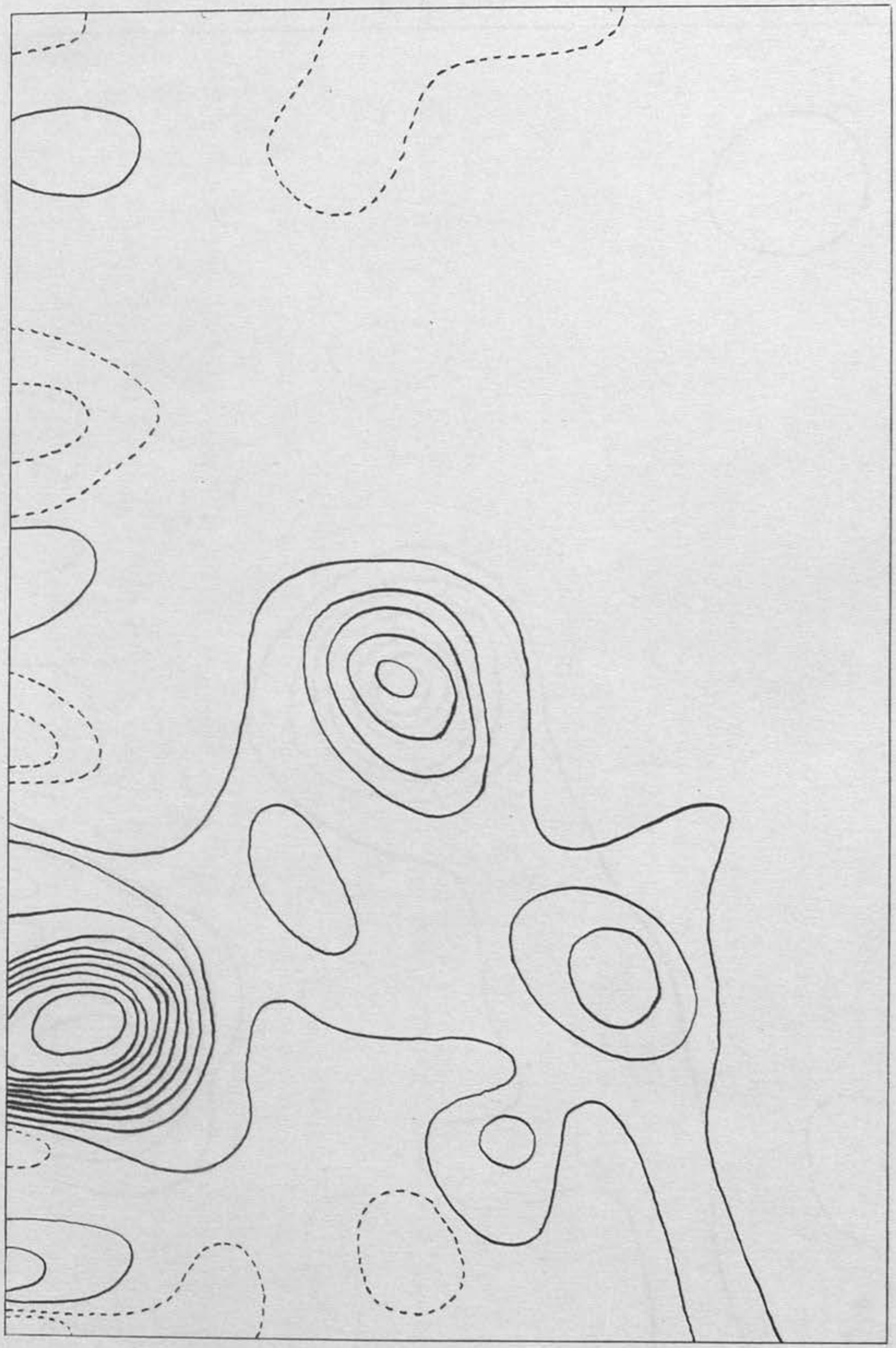
Z = 2/24

Fig 3 (iv)



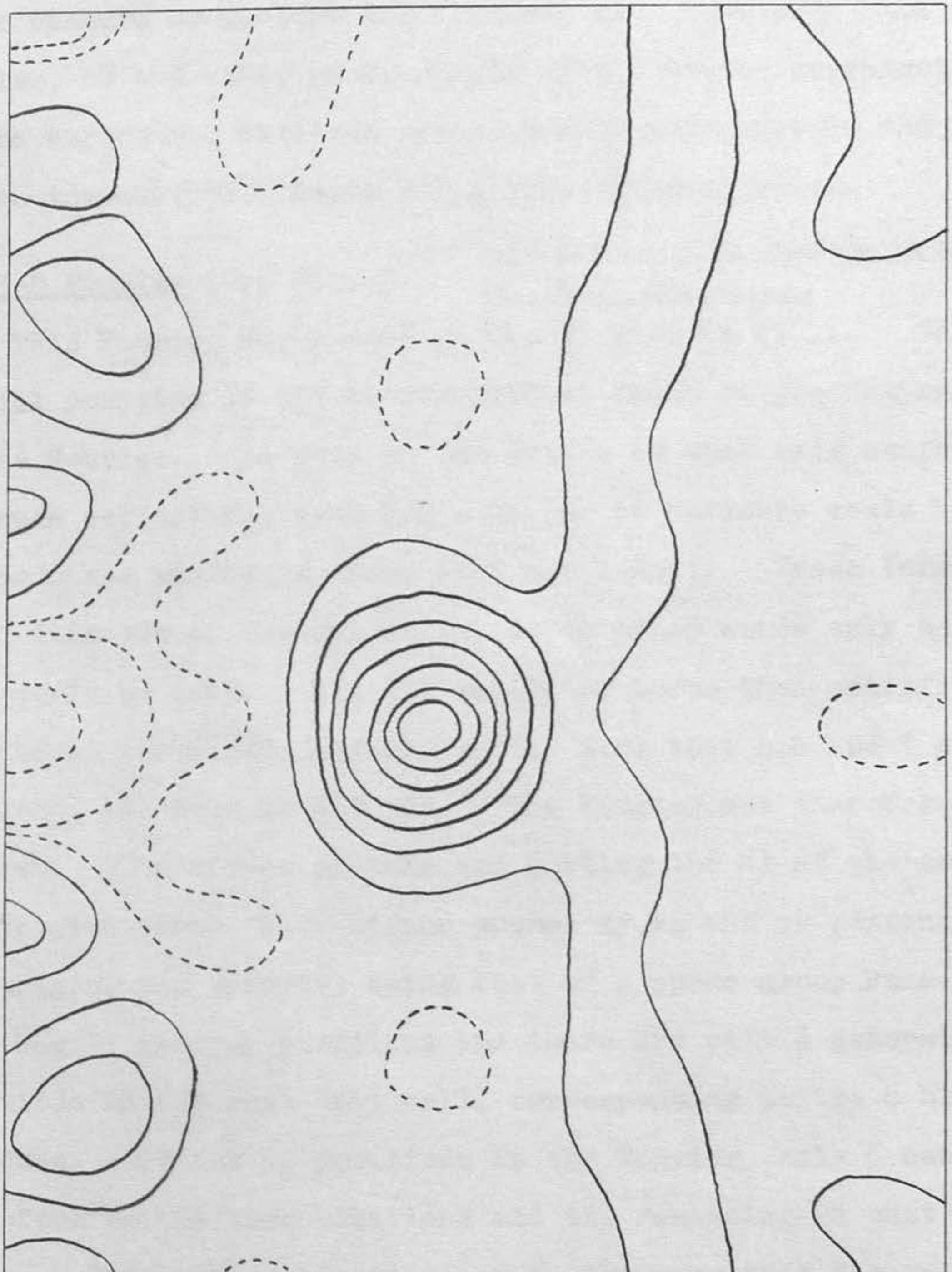
Z = 3/24

Fig 3 (v)



Z = 4/24

Fig 3 (vii)



$Z = \frac{6}{24}$

with a superimposed background of light atom vectors, which might obscure or distort the Ni-light atom vectors. The Fourier, on the other hand, should give a better representation of the structure, although errors due to poor phasing and series termination effects etc., were to be expected.

1st 3-D Fourier (see Fig. 3)

i.e. Calculation of the electron density in three dimensions

This Fourier was phased on the Ni atom at 0,0,0. The special position of the Ni resulted in false or pseudosymmetry in the Fourier. An atom at the origin in Aba2 only contributes to those reflections with $h+k = 2n$, so no estimate could be made of the phase angles of terms with $h+k = 2n+1$. These terms had to be left out of the summation, or in other words only half the data could be used. All the remaining terms then satisfied the conditions for a face centred cell: i.e. that h,k and ℓ should be either all even or all odd. The Fourier was therefore face-centred. The effect of this and putting the Ni at the origin, was to give three false mirror planes xy,xz and yz passing through the origin, the symmetry being that of a space group Fmmm. Now Fmmm has 32 general positions and there are only 8 general positions in the real unit cell, corresponding to the 8 histidine residues. Of the 32 positions in the Fourier, only 8 can therefore be the true positions and the remaining 24 must be false. The problem was to separate the true from the false peaks. Considering a single histidine residue, any one of 32 peaks could initially be taken to correspond to a certain atom of histidine, but this choice automatically fixed the positions of the rest of the/

the atoms. In a sense this initial freedom of choice is equivalent to an arbitrary decision about the signs of the orthorhombic axes.

The presence of false mirror planes resulted in some complications. Peaks near or on the xy, xz or yz planes were distorted by reflection in these planes, a peak exactly on one of the planes having its electron density doubled. More severe distortion was present in peaks near one of the axes, a peak exactly on an axis having its electron density multiplied by 4. The positions of such peaks could not be determined unambiguously.

It was fortunate that in $\mathrm{Ni(histidine)_2}$ there is a 5-membered imidazole ring which could be easily recognised in the Fourier. It was this feature that proved to be the key to the structure.

The Fourier is shown in Fig. 3 for $x, o-\frac{1}{4}$; $y, o-\frac{1}{2}$; and $z, o-\frac{1}{4}$. Contours are drawn at intervals of $\frac{1}{2}$ electron per $\mathring{A}^3$. The light atom peaks are of about the correct density, although the peak at $o\ \frac{1}{2}\ o$ (in the expected position of the water molecule) is rather high at 8.7 ε's $\mathring{A}^{-3}$.* This is probably due to series termination and diffraction effects, etc., causing a build-up of errors at $o\ \frac{1}{2}\ o$. Strong diffraction ripples surround the Ni atom and tend to distort those light atom peaks near to the Ni. In order to visualise the Fourier clearly, a 3-dimensional model was made on a cork baseboard using wires and pieces of plastic. A model of a histidine molecule was made on the same scale, and attempts/

---

* This should read e. $\mathring{A}^{-3}$, and hereafter.

attempts made to fit the histidine atoms on the Fourier peaks. It rapidly became obvious that there was only one set of peaks which would fit a planar imidazole ring. Moreover one peak was at the correct distance (~ 2.0 Å) from the Ni for a nitrogen. This peak was therefore assigned to N_2, and there was a peak in the correct position for C_3. There were also peaks in reasonable positions for the carboxyl group, C_2 and N_1, but at this stage there were too many ways of assigning these peaks to be sure of the correct structure. However there could be no doubt that the imidazole ring and C_3 fitted very well on to the peaks. It was therefore decided to phase a second Fourier on the Ni, the 5 atoms of the imidazole ring and C_3. First the co-ordinates of the peaks were measured using Booth's method [47].

The signs of the co-ordinates of one atom could be assigned quite arbitrarily, and so the co-ordinates of C_5 were taken all positive. This fixed the signs for all other atoms. C_6 seemed to lie very close to the x axis and it could not be decided on which side it lay. C_6 was therefore placed on the x-axis hoping that when the false symmetry was broken, the peak density would move away from the axis. Similarily N_2 was near the xy plane, and so its z/c value was taken to be zero. The co-ordinates derived are given in Table 5.

Second 3-D Fourier

Structure factors were calculated for Ni, N_2, C_5, N_3, C_6, C_4 and C_3 in the positions found from the 1st 3-D Fourier. Temperature/

Temperature factors were guessed at B = 4.0 $Å^2$. for all atoms. The R factor ($\Sigma|\Delta|/\Sigma|F_o|$) was 42%, and the agreement shown between $|F_o|$ and $|F_c|$ over $\sin^2\theta$ ranges, proved that the guessed temperature factors could not be far wrong.

The phases angles from this calculation were combined with the observed F's and a Fourier calculated. A simple weighting scheme was used which omitted all excessively high F_o values where $F_o > 5\ F_c$. $\frac{1}{8}$th Of the unit cell was covered (x,y,z : 0- $\frac{1}{2}$) and sections were taken perpendicular to z at intervals of c/24. Values were computed at intervals of $^a/_{60}$ along x and $^b/_{40}$ along y.

The Fourier showed very promising features. All the seven atoms put into the S.F. calculation had good peaks of higher electron density than the 1st 3-D Fourier, as would be expected. Moreover the false peaks corresponding to these atoms in the 1st Fourier had disappeared completely and were replaced by regions of negative electron density. In the 1st Fourier there was a false two-fold axis, $\frac{11}{44}$z. This axis passed through the centre of each section of the 2nd Fourier and the fact that it was no longer a two-fold axis could be seen at a glance at each section. Peaks corresponding to the remaining atoms (C_1, C_2, O_1, O_2, N_1 and O_3) were all found in reasonable positions, but they all had lower electron densities. Also each of these atoms not put into the S.F. calculation, had a false or "ghost" peak of about half the density related by the two-fold axis. There was therefore a certain amount of "residual pseudosymmetry" left in the Fourier.

The following table lists the peak electron density for each atom/

atom in the 2nd 3-D Fourier:-

Atoms put into S.F.'s	Peak electron density (ε's $Å^{-3}$)
Ni	66.7
N_2	12.9
N_3	12.6
C_3	10.4
C_4	10.4
C_5	10.7
C_6	8.5
Atoms not put into S.F.'s	
O_1	7.5
O_2	6.1
O_3	8.6
C_1	4.9
C_2	4.9
N_1	7.5

The density of atoms not put into the S.F.'s was on average about $\frac{2}{3}$rds of the density of atoms put into the S.F.'s. This result was expected as any atom put into an S.F. calculation for an acentric structure, will tend to alter the phases in such a way as to produce a peak at the same position in the Fourier synthesis. The height of these peaks - well above the atomic number - was encouraging. Even more encouraging was the fact that peaks of about the correct relative densities were in reasonable positions for the rest of the histidine molecule, and their "ghost peaks" had only half the electron density. There could be little doubt at/

at this stage that the trial structure was correct.

The positions of maximum peak density were calculated using Booth's method [47]. According to Donohue [48], a "double shift" rule should be applied in acentric Fourier refinement. This rule was not used at this stage since the original positions from the 1st 3-D Fourier were much less reliable than those from the 2nd 3-D Fourier. Shifts were noted for C_6 which was originally placed on the x-axis and N_2 which was on the xy plane. O_3 Also moved slightly from z = ·500 to ·498. The co-ordinates so derived were used to calculate the 1st 3-D $(F_o - F_c)$ map.

1st 3-D $(F_o - F_c)$ map

All atoms in the structure (except hydrogen) were put into this calculation, and all temperature factors were set at $B = 4.0\ Å^2$. The R factor was 19.7% - a considerable improvement from the last S.F. calculation. The $(F_o - F_c)$ synthesis was computed in the same way as for the 1st 3-D Fourier, and the same weighting scheme was used.

The difference map showed a very smooth background electron density of between + ·4 and - ·4 ε 's $Å^{-3}$. There were occasional peaks and hollows up to a maximum of about ± 1 ε $Å^{-3}$ in the neighbourhood of histidine atoms, but the major features were a large hollow of -3.7 ε 's $Å^{-3}$ at ·5Å along x from the Ni, and a spherical negative peak of -3.2 ε's $Å^{-3}$ at O_3. In addition there were prominent ripples surrounding the Ni atom. The strong negative peak near Ni was taken to indicate anisotropic vibration of/

of the Ni, although the absence of a corresponding high positive peak was rather puzzling. The negative peak at O_3 was due to the low B value of 4.0 $\mathring{A}^2$ given to O_3.

Shifts were calculated in the three axial directions for all atoms from the formula:- [49]

$$\Delta x = \frac{\left(\partial D / \partial x \right)}{2 p \cdot \rho_{obs.}}$$

where Δx is shift in Å along x

$\partial D / \partial x$ is gradient on $(F_O - F_c)$ map $(\varepsilon\ \mathring{A}^{-4})$

p is a constant $(\mathring{A}^{-2})$

ρ_{obs} is the electron density on an F_O synthesis $(\varepsilon\ \mathring{A}^{-3})$

The gradients were measured roughly at the position of each atom, ρ_{obs} was the peak density taken from the 2nd 3-D Fourier and a value $p = 5.0\ \mathring{A}^{-2}$ was taken for all atoms. The shifts so calculated varied from zero to a maximum of ·04 Å (C_5), but on average were about ·015 Å. The "double shift" rule [48] was applied, and the co-ordinates so derived are given in Table 5. The values of $(|F_O| - |F_c|)$ at each atom were mostly small $(< \cdot 5\ \varepsilon\text{'s}\ \mathring{A}^{-3})$, and so the B values were not altered. The value for O_3 was raised to $B = 6 \cdot 0\ \mathring{A}^2$ however.

TABLE 4

Solution and refinement of Ni (histidine)$_2$. H_2O

	R%
1st 3 - D Fourier phased on Ni	
Structure Factors	42.0
2nd 3 - D Fourier phased on 7 atoms	
Structure Factors	19.7
1st 3 - D $(F_O - F_c)$ map phased on all atoms	

Least Squares Refinement

Round	Hydrogens	Temperature Factors	O3 shift	k in kFO	$10^{-4}\sum w\Delta^2$	R%
	None	All isotropic		7.468	306	17.65
1						
	"	" "	-.17Å	7.605	268	15.00
2						
	6H	Ni anisotropic rest isotropic	+.11Å	7.778	257	13.92
3						
	"	"	-.12Å	7.798	230	13.35
4						
	"	11 atoms aniso. N3,O3 and H atoms isotropic	-.009Å	7.742	222	13.06
5						
	"	"	-.018Å	7.740	188	11.95
6						
	"	"	nil	7.692	191	12.40
7						
			+.006Å	7.662		

TABLE 5

Coordinates after interpretation of 1st 3-D Fourier

Atom	x/a	y/b	z/c
Ni	.0000	.0000	.0000
C3	.1845	-.1323	-.1250
C4	.2060	-.0250	-.0300
C5	.1803	.1240	.0833
C6	.2803	.0000	.0000
N2	.1356	.0275	.0000
N3	.2617	.1011	.0425

Coordinates after interpretation of 1st 3-D $F_o - F_c$ map

Atom	x/a	y/b	z/c
Ni	.0000	.0000	.0000
C1	.0840	-.1828	.1068
C2	.0916	-.1810	-.0931
C3	.1869	-.1369	-.1284
C4	.2046	-.0322	-.0436
C5	.1757	.1176	.0739
C6	.2801	.0186	-.0022
N1	.0284	-.1188	-.1738
N2	.1356	.0311	.0034
N3	.2612	.1023	.0553
O1	.0259	-.1182	.1757
O2	.1200	-.2489	.2087
O3	.0000	.0000	.4973

(e) Refinement of the Structure

The co-ordinates, with shifts applied from the 3 D $(F_o - F_c)$ map, were now refined by least squares. The program used on Atlas was SFLS Diamond/Harding (see page 97) which uses a block diagonal approximation. The course of least squares refinement is shown in Table 4.

Unfortunately it was not possible to omit the refinement of the z parameter of Ni, and at the same time refine its temperature factor as should be done. In fact z parameter shifts were computed for Ni but not applied. By symmetry the x and y parameter shifts for Ni and O_3 were zero. In structures with floating origins, such as this one, the off-diagonal elements between co-ordinates of different atoms may not be negligible, and a full matrix refinement should be used if possible. However no full matrix SFLS program was readily available. The slow convergence of the refinement was probably due to this.

The f-curves used were as follows:-

O_1, O_2 (carboxyl)	-	$f_{O\frac{1}{2}-}$ (average of f_O and f_{O-})	[50]
O_3 (water)	-	f_O	[50]
N_{1-3}	-	f_N	[51]
C_{1-6}	-	f_C	[52]
Ni	-	$f_{Ni^{++}}$ without anomalous dispersion correction	[53]

The weight, w, given to each term was a function of F_o such that if F_o (absolute scale) $\leqslant$ 80 then w = 1, and otherwise

w/

$w = (^{80}/F_o)^2$. This resulted in the high values of F_o being given reduced weights, while all the low values had a constant weight of 1. It was rather an insensitive scheme, not bearing very much relation to the probable errors in F_o, but it was the only one available at the time.

Throughout the refinement, co-ordinates and temperature factors of all atoms other than the hydrogens, were refined. The output of one round was always input to the next without application of any "partial shift factors".

In Rounds 1 and 2 shifts of about ·012 Å were computed (but not applied) for the Ni z parameter. In all subsequent rounds the shifts were negligible. The water molecule, O_3, showed considerable oscillation in its z parameter and 'B' value, as may be seen in Table 4. This was probably due to O_3 not occupying a fixed position in the crystal, but being statistically distributed over a small region surrounding its final position. This interpretation was supported by its high temperature factor of 5.3 $Å^2$, and the wide positive peak found in the (F_o-F_c) map, (see page 36). All temperature factors were isotropic and no H atoms were included in Rounds 1 and 2. In Round 1 the average shift was $\sim$ ·020Å rising to a maximum of ·08Å for C_4 (except for O_3). The 'B' shifts were large and negative, averaging $\sim -1{\cdot}0Å^2$. Round 2 showed a smaller average shift of $\sim$ ·017Å with a maximum of ·04Å for C_2 and the 'B' shifts had fallen to an average of ·1$Å^2$.

At this stage it was decided to put those H atoms into the structure/

structure, whose positions could be fixed chemically. It was essential to do this before allowing anisotropic vibrations to an atom with hydrogen attached, as the vibration ellipsoid might be artifically elongated in the direction of the H atom. Positions were calculated for all except the two H atoms on N_1 and the one unique H atom on O_3. 'B' values equal to the isotropic 'B' values of the heavy atom to which the hydrogen was attached, were given to each H atom. Six such H atoms were included in Rounds 3 and 4 and the Ni allowed to become anisotropic. The average shifts in co-ordinates were less than ·008 Å and in 'B' values less than ·1 Å^2. The drop in R of - ·86% over Rounds 3 and 4 was rather low and disappointing, considering that the effect of the 6 H atoms and the Ni anisotropy should have made their effects felt on R. However the drop in $\sum \omega \Delta^2$ was 13·7%.

In Rounds 5, 6 and 7 all but N_1 and O_3 (whose hydrogen atoms were not included) and the hydrogens were allowed anisotropic vibrations. As far as Round 5 the refinement seemed to be proceeding well, but Round 6 produced a 1·6% rise in $\sum \omega \Delta^2$ and a ·45% rise in R. This was probably the result of two factors:

(i) Lack of full matrix treatment in the refinement of an acentric structure with atoms in special positions. The off-diagonal terms which were not taken into account may not have been negligible.

(ii) Use of an f-curve for the Ni^{++} ion without allowance for anomalous/

anomalous dispersion. The dispersion correction would subtract approximately 3 electrons from f, and would therefore have a large effect on the anisotropic vibrations of Ni.

The co-ordinate shifts for Rounds 6 and 7 were on average about two-thirds of the shifts of Round 5. The maximum shifts were ·007 Å (C_3, C_6, N_2) for Round 6 and ·010 Å (C_6) for Round 7. There was quite a significant fall in scale factor, K (applied to F_o), of 1·3% over Rounds 5-7. The average shift : estimated standard deviation (E.S.D.) ratio was about ·2 in both Rounds 6 and 7 and the maximum shift ratios were:

Round 6	·67(C_4),	·79(C_6),	·53(C_3)
Round 7	1·0(O_1)	1·0(C_6)	·75(C_4)

The ratios for Round 7 seem to be slightly greater, but nevertheless the co-ordinate E.S.D. of each atom was reduced to nearly half its previous value over the three last rounds, the ratio from one round to the next being fairly constant for all atoms. The values relative to those of Round 7 were:-

Round	5	6	7
E.S.D. ratio	1·64-2·15	1·15-1·27	1·00

It is quite clear that parameters in this refinement have not converged properly to their true values, and further work remains to be done before the results can be published. A refinement using a corrected f curve for Ni^{++}, and preferably a full matrix least squares treatment, would probably give better convergence. However considering the average shift: E.S.D. ratio is ·2, the light atom positions/

positions are probably good enough to describe the structure with reasonable accuracy.

The final co-ordinates, E.S.D.'s and vibrations output by Round 7 are given in Table 6. A list of observed and calculated structure factors (in the form A_o, B_o, A_c, B_c) is given in Appendix I. They were calculated with the parameters output by Round 6 and therefore correspond to R = 12·4%.

Final 3D(F_o-F_c) map.

This was computed with the parameters output by Round 6 (R = 12·4%) omitting the hydrogens. The R factor was 14·3%, and this rise of 1·9% may therefore be taken as the contribution of the 6 hydrogens to R. The hydrogens all had positive electron densities of about ·25 ε's $\mathring{A}^{-3}$, but many of the peaks had very irregular shapes, and the peak maxima were often not in the expected positions. The major features were near the Ni atom and at O_3. O_3 occurred on a peak of about +1 ε $\mathring{A}^{-3}$ on the difference map. This peak was very elongated along y and also slightly along z, but was very narrow in the x direction. This agrees quite well with the high vibrations of O_3 in the y and z directions (see Table 6). The positive electron density may have been due to the omission of the hydrogen attached to O_3, and also perhaps due to artificially high vibrations given to O_3 because of the uncertainty in its position.

The features in the difference map around Ni were rather peculiar, and were probably due to the poor f curve used for Ni, and/

and the resulting distortions in the anisotropic temperature factors. Ni itself occurred at $\Delta = 0$, but there were well defined ripples of wavelength 1 Å along the y direction. Thus there were peaks of about $-1\,\varepsilon\,\text{Å}^{-3}$ at ·5 and 1·5 Å, and $+1\,\varepsilon\,\text{Å}^{-3}$ at 1·0 Å along y. Along x, the ripples were less well defined but a positive peak of $+1\,\varepsilon\,\text{Å}^{-3}$ occurred at ·5 Å. Along z there were no comparable features. The whole pattern rather suggested strong anisotropic vibration of Ni, but the ripples were very sharp and narrow.

TABLE 6

Ni (histidine)$_2$.H$_2$O Final Coordinates and E.S.D.'s.

Atom	x/a	10^5E.S.D.	y/b	10^5E.S.D.	z/c	10^5E.S.D.
Ni	.00000	-	.00000	-	.00000	-
C1	.07949	52	-.18436	58	.11484	132
C2	.09566	55	-.17878	64	-.08143	133
C3	.18802	61	-.13560	85	-.11916	150
C4	.20284	51	-.03624	68	-.04256	138
C5	.17216	59	.11609	79	.06615	152
C6	.28124	48	.01700	73	-.00769	229
N1	.02944	42	-.11643	55	-.17885	140
N2	.13480	38	.03344	47	.00344	163
N3	.25979	49	.10811	63	.05709	120
O1	.02566	36	-.12070	55	.17534	90
O2	.11983	39	-.24816	51	.20066	95
O3	.00000	-	.00000	-	.47795	290

Hydrogens

Atom	x/a	y/b	z/c	B (Å)	Attached to
H1	.0859	-.2499	-.1328	2.46	C2
H4	.2016	-.1326	-.2518	3.31	C3
H5	.2309	-.1897	-.0639	3.31	C3
H6	.1407	.1835	.1159	3.24	C5
H7	.3051	.1627	.0977	3.26	N3
H8	.3475	-.0042	-.0234	3.20	C6

Vibrations Temp. Factor = $\exp-(h^2B_{11}+k^2B_{22}+l^2B_{33}+klB_{23}+lhB_{31}+hkB_{12})$

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{31}	B_{12}
Ni	.00267	.00586	.01426	.00000	.00000	-.00039
C1	.00192	.00060	.02388	.00423	.00112	-.00167
C2	.00218	.00190	.01929	-.00385	.00004	-.00004
C3	.00216	.00744	.01579	.00033	.00431	.00441
C4	.00121	.00402	.02609	.01031	.00204	.00104
C5	.00169	.00445	.02083	.00152	-.00549	.00118
C6	.00075	.00843	.02111	.00785	.00218	-.00154
N2	.00079	.00343	.01941	-.00208	-.00047	-.00072
N3	.00193	.00792	.02025	.00896	-.00607	-.00605
O1	.00094	.00956	.01099	.00550	-.00008	-.00013
O2	.00226	.00383	.01832	.00639	.00412	.00178
N1	B (Å^2) = 2.91					
O3	B (Å^2) = 5.25					

(f) Final calculations on the structure.

(i) Bond lengths and angles

Bond lengths and angles were computed using a program written by O.S. Mills (see page 98). The E.S.D.'s of bond lengths were calculated from co-ordinate E.S.D.'s (ignoring covariances) using Fraser Program 3/2. They are given in Table 7.

(ii) Calculation of best planes and projections

These were computed using a molecular geometry program (see page 97) which calculated the best planes by minimising the squares of the deviations from the plane.

Best plane of imidazole ring (Fig. 4(i)).

Equation: $+ \cdot 0455x - 5\cdot 073y + 7\cdot 111z + \cdot 1228 = 0$

Best plane of carboxyl group, i.e., O_1, O_2, C_1, C_2 (Fig. 4(ii)).

Equation: $+ 11\cdot 30x + 8\cdot 505y + 1\cdot 118z + \cdot 5355 = 0$

Best plane through N_1, N_2', O_1', N_2 (Fig. 5(i)).

Equation: $+ 2\cdot 064x - 8\cdot 288y + 5\cdot 869z - \cdot 003 = 0$

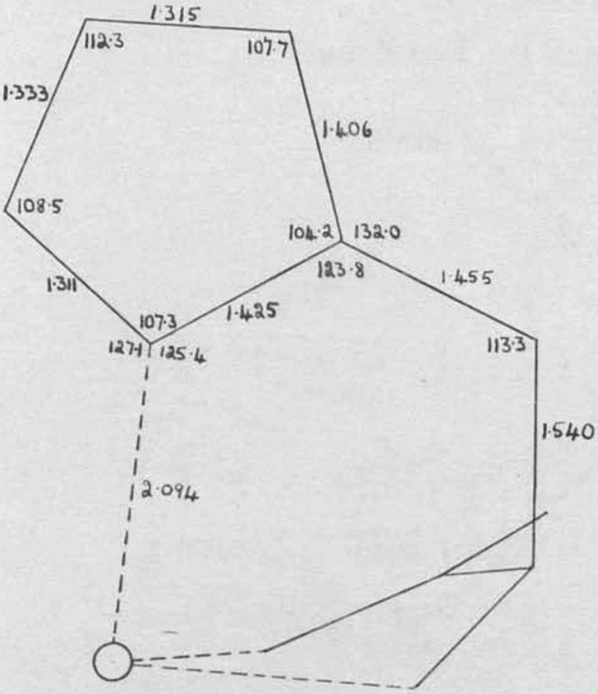
The plane N_1', N_2', N_2, O_1 is related by symmetry.

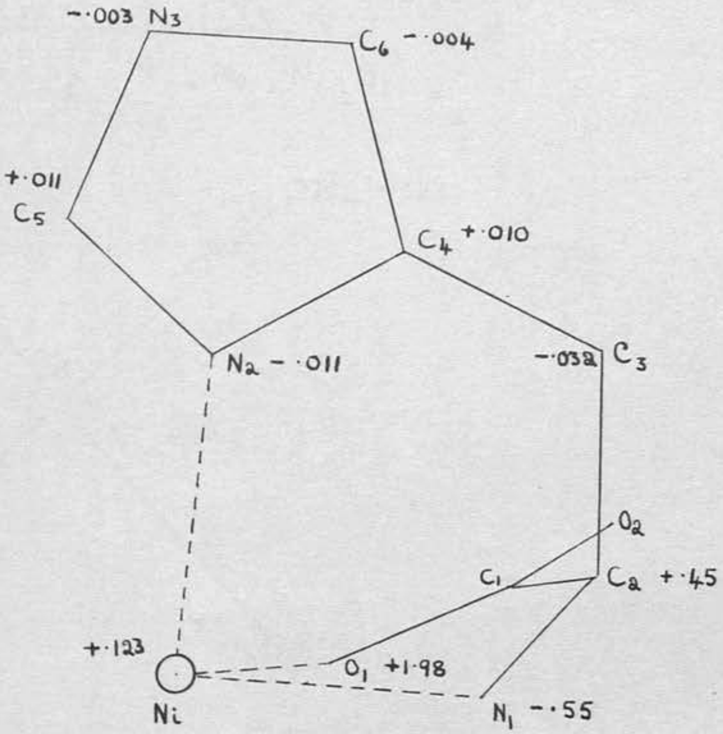
Best plane through N_1, O_1, N_1', O_1' (Fig. 5(ii)).

Equation: $+ 14\cdot 649x + 3\cdot 415y = 0$

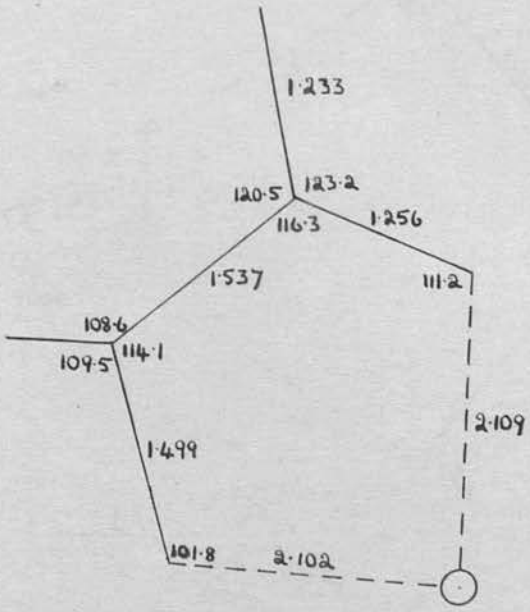
Fig 4

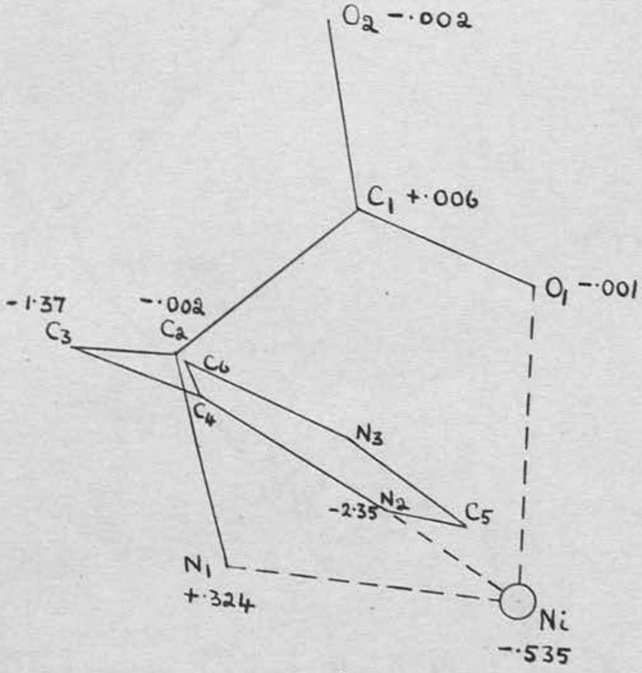
(i) Best Plane of N_2, C_5, N_3, C_6, C_4





(ii) Best Plane of O_1, O_2, C_1, C_2





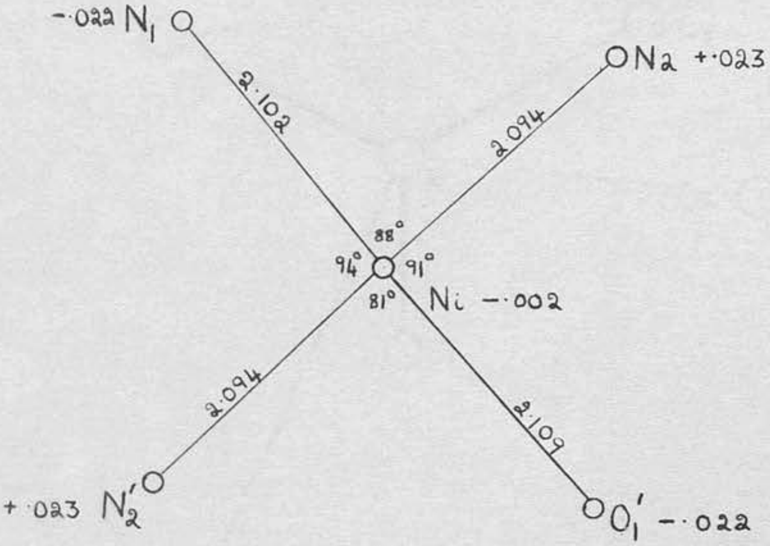
Bond Lengths (Å)
Angles (degrees)

Distances (Å) from
Best Plane

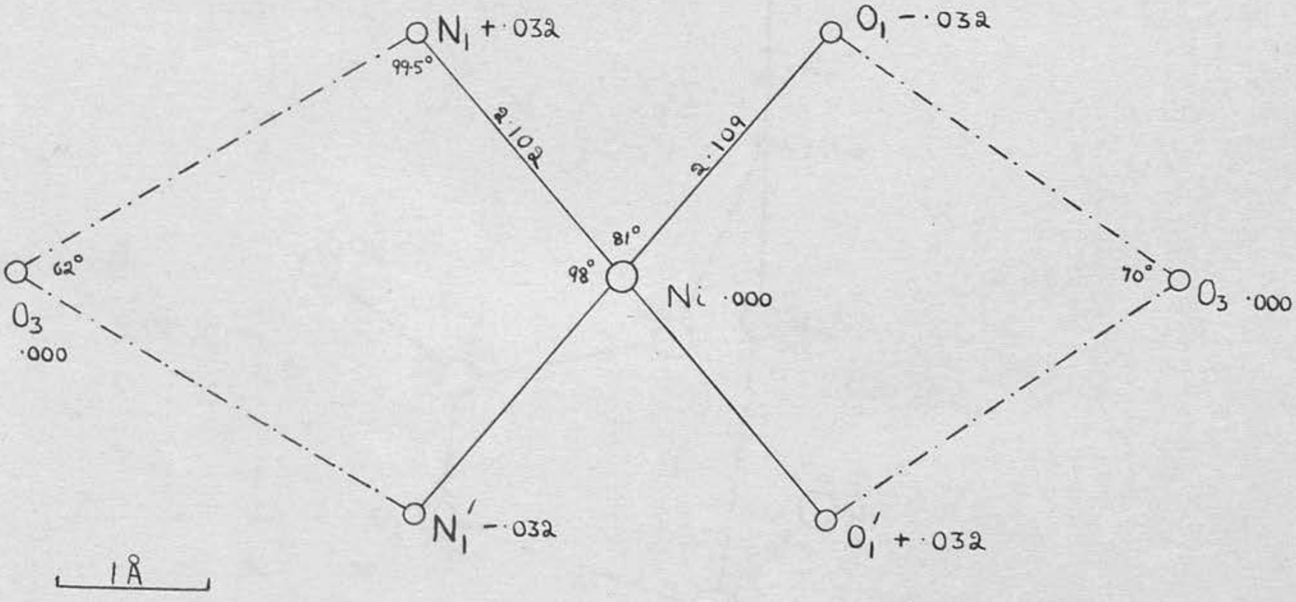
Fig 5

Coordination of Ni

(i) Best Plane of N_1, N_2, N_2', O_1'



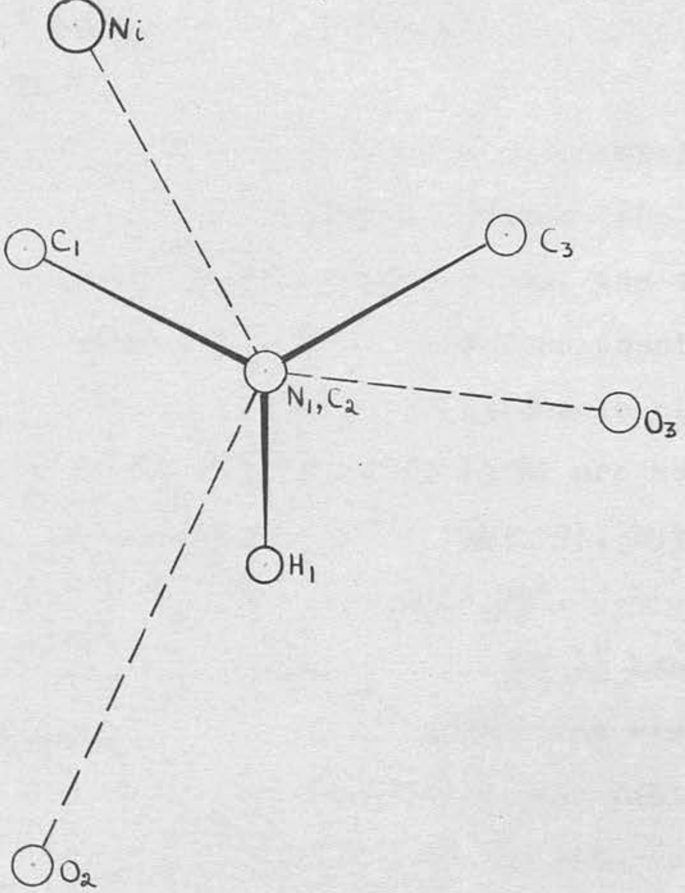
(ii) Best Plane of N_1, O_1, N_1', O_1'

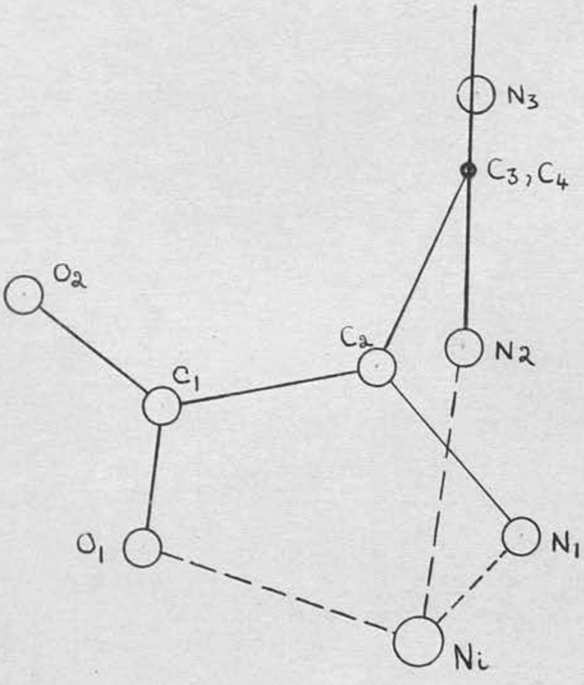


Bond Lengths and Distances from Best Plane in Å

Fig 6

(i) Projection along $N_1 - C_2$





(ii) Projection of histidine residue along $C_3 - C_4$

(g) Description and Discussion of Structure.

Nickel co-ordination

The co-ordination is very nearly regular octahedral. Ni lies almost exactly on all three octahedral planes (see Fig. 5). O_1 and N_1 show a slight twist from the best plane, the deviations from the plane being about 3(E.S.D.) and therefore possibly significant. N_1 lies slightly towards the imidazole ring and O_1 away from it. The angles made by bonds to Ni are mostly within 3° - 4° of the true octahedral values (see Table 7), but $N_1 \widehat{Ni} O_1 = 81°$, $N_1 \widehat{Ni} N_1' = 98°$ and $O_1 \widehat{Ni} O_1' = 99°$.

The Ni - N_1 (2.102 Å) and the Ni - N_2 (2.094 Å) bond lengths do not differ significantly, and agree well with the average literature value for Ni - N (amino) of 2.104 Å (see Table 2). The value of 2.109 Å for Ni - O_1 agrees with the literature trend which shows Ni - O (carboxyl) bonds (av. 2.13 Å) to be slightly longer than Ni - O (carbonyl) (av. 2.01 Å) or Ni - O (water) (av. 2.06 Å).

Imidazole Ring

The imidazole ring is planar within experimental error, all the five atoms lying at distances less than 1 E.S.D. from the best plane (see Fig. 4(i)). C_3 however lies at ·032 Å from this plane which is about 3 E.S.D.'s and therefore possibly significant. The Ni atom is ·123 Å from the imidazole plane (cf. a distance of ·15 Å was found in DL(histidine)$_2$ Zn.5 H_2O [3].) The distances within/

within the ring are compared with the average found over the two zinc complexes [3,4] in Table 7. All are within 2 E.S.D.'s of the average except C_6-N_3 which is ·076 Å short (C_4-C_6 is rather long). It is also ·045 Å shorter than the value in histidine hydrochloride [14]. This is certainly significant, and may well be due to the rather special position of C_6 near the plane, x = 0. There is a marked inequality of the angles $C_3 \hat{C}_4 C_6$ and $C_3 \hat{C}_4 N_2$ (132° and 124° respectively) - very nearly the same as in histidine hydrochloride [14], but different from the two zinc complexes where the angles are nearly equal. This would help to confirm Kretsinger, Cotton and Bryan's impression that there is considerable flexibility in this bond angle.

Carboxyl Group

O_1, C_1, O_2 and C_2 are all accurately coplanar (see Fig. 4(ii)), but N_1 lies ·324 Å from this plane. The "peptide group" is therefore not planar, as has been found also in L Zn(histidine)$_2$ 2H_2O [4] and also to a smaller extent in histidine hydrochloride [14]. The bond lengths are compared in Table 7. Only C_1-O_1 (·035 Å long) and C_1-O_2 (·023 Å short) are without 1 E.S.D. of the average values, but C_1-O_1 agrees well with the histidine hydrochloride value of 1·252 Å. The angle $O_1 \hat{C}_1 C_2$ is smaller by about 4° and $C_1 \hat{C}_2 N_1$ larger by about 4° than those of other determinations, again suggesting some flexibility in bond angles.

Histidine/

Histidine conformation

The conformation of the individual histidine molecule is similar to that in the two zinc complexes, except there has been a slightly greater rotation about C_3-C_4 from the most favourable situation in histidine hydrochloride (cf. Fig. 6 (ii)) and Fig. 5 of Harding and Cole [3]. Assuming the "peptide" group to be roughly planar and the imidazole ring and C_3 to be coplanar, the conformation can be varied by rotation about C_2-C_3 and/or C_3-C_4. The dihedral angle between the imidazole ring and the plane of C_2, C_3 and C_4 is 23·0°. (Cf. 40° in the zinc complexes and 121° in histidine hydrochloride). This rotation is necessary to bring N_2 into a position suitable for co-ordination to the metal atom. (Note that in both cases the imidazole ring does not quite rotate far enough to bring the metal atom into its own plane). In the nickel complex the rotation has been larger than in the zinc complexes, because the Ni atom has moved closer to O_1 (the Ni-O_1 bond being much stronger). In contrast, there seems to have been very little rotation about the C_2-C_3 bond in all determinations, although there seems to be no obvious reason why such rotation should not take place. The angle between the plane of the carboxyl group and the plane of C_2, C_3 and C_4 is 56·1° in the nickel complex.

N_1-C_2 Projection

This projection is given in Fig. 6(i) and should be compared with/

with Figs. 2 and 3 of Donohue and Caron [14]. In histidine hydrochloride and the two zinc complexes, the conformation along the N_1-C_2 bond is almost exactly staggered. Fig. 6(i) shows that in projection the Ni atom deviates by 26° from the staggered position. This must be the result of fewer degrees of freedom in the nickel complex, where N_1, N_2 and O_1 all bind strongly to an octahedral Ni atom. In the zinc complexes there is greater freedom since O_1 binds weakly. The energies involved in co-ordination are, of course, much greater than those of hydrogen bonding, or of maintaining a staggered conformation. Fig. 6(i) shows that O_2 takes up a position approximately tetrahedral to Ni and C_2. The slightly long N_1-H_2....O_2 hydrogen bond (2·99 Å) could be connected with the departure from staggered conformation.

Packing and Hydrogen Bonding

Figs. 7 and 8 illustrate the packing and hydrogen bonding. The structure is dominated by hydrogen bonds, and Van der Waals' interactions play only a minor part in holding the crystal together. Considering a single Ni(histidine)$_2$ molecule, it can be regarded as being surrounded by 14 others as follows:

I. There are 4 A face-centred neighbours, (I), related by two-fold screw axes, at a distance of 7·5 Å (Ni-Ni). Each of these is bound by one hydrogen bond (2·99 Å) from either N_1 or O_2 of the molecule under consideration. The nitrogen binds to O_2(I) and the oxygen to N_1(I) of the neighbour. As may be seen in the C-axis projection the carboxyl groups of neighbouring molecules are/

are approximately parallel, and they therefore form parallel "sheets" extending along the c axis directly hydrogen bonded to each other.

II. 4 molecules, (II), related by the b glide, are centred 10·0 Å away at the same 'z level'. Each of these is bound by one hydrogen bond (2·85 Å) from N_3 to O_2 (II) or from O_2 to N_3 (II). These four bonds are roughly in a plane at right angles to each other, and this tends to prevent any movement in the plane normal to z.

III. 4 molecules, (III), related by the a glide, are centred at 8.5 Å away, but are not directly bound by hydrogen bonds. However their imidazole rings are quite accurately parallel to the imidazole rings of the molecule under consideration, and the perpendicular distance between the rings is 3.5 Å (see a-axis projection). They are therefore in Van der Waals" contact and form "sandwiches" preventing movement along the z direction.

IV. 2 molecules, (IV), are at 7.7 Å (cell translation) along z, above and below. They are not directly bonded but are held in position by indirect hydrogen bonds to molecules I, Van der Waals" contact to molecules III, and by hydrogen bonding to the water molecule, O_3, situated in the empty space between Ni atoms along the z-axis.

Not counting the hydrogen bonds involving water (O_3), there are only two unique hydrogen bonds in the structure, i.e.

$N_1 - H_2$................O_2(I) and
$N_3 - H_7$................O_2(II)

The $N_1 - O_2$(I) distance is 2·99 Å and $N_3 - O_2$(II) is 2·85 Å, both within the limits for a N(ammonium) - H..........O bond, the average literature value being 2·88 Å [54]. O_2(II) lies in the expected position for a hydrogen bond with H_7 of N_3. It is only ·28 Å out of the plane of the imidazole ring (see Fig. 8) and $C_6 \hat{N}_3 O_2(II) = 119°$ and $C_5 \hat{N}_3 O_2(II) = 131°$. O_2(I) is in a favourable position for bonding to H_2 of N_1. The $C_2 \hat{N}_1 O_2(I)$ angle is 109°, exactly right assuming N_1 to be tetrahedral.

The situation of the water molecule, O_3, may be studied by reference to Fig. 5(ii). It fills the gap between molecules along the z-axis, and lies almost half-way between the Ni atoms. There are four atoms within hydrogen bonding distance:- N_1 and N_1' at 3·03 Å and O_1 and O_1' at 2·89 Å. There are no hydrogens available on O_1 and therefore the O_3 hydrogens must be used. The $O_1 \hat{O}_3 O_1'$ angle is 70°, and if both O_1 and O_1' are bonded at the same time (i.e. if the space group symmetry is strictly obeyed), the hydrogens must deviate from the $O_3 - O_1$ line by about 17·5° (assuming $H \hat{O} H = 105°$). H_3 on N_1 is available for hydrogen bonding but $C_2 \hat{N}_1 O_3 = 143°$ and $Ni \hat{N}_1 O_3 = 99·5°$ (N_1 cannot, of course, accept a hydrogen from O_3). H_3 therefore deviates quite far from the $N_1 - O_3$ line, and this is probably the explanation of the slightly longer than average bond length of 3·03 Å. O_3 has also two contacts of 3·32 Å with C_6 of two neighbouring imidazole groups,/

groups, and O_3 lies almost exactly in the plane of these rings (see Fig. 8).

There is a certain doubt about the exact position of O_3. During least squares refinement its z parameter oscillated badly and its temperature factor of 5·3 Å ^{2} is much higher than that of any other atom. Although, according to the space group, it must lie on the 2-fold axis, there is no reason why this symmetry should be strictly preserved. It is quite possible to imagine that it is statistically distributed over a small volume of space and the orientation of its hydrogens is variable. This is supported by the evidence of the final $(F_o - F_c)$ map (see page 36) which showed a positive peak of 1 ε $Å^{-3}$ elongated along y and z. There was no elongation along x, and this is very probably the result of its contacts with C_6 which would prevent much movement along x.

A possible explanation of these results is that O_3 is not symmetrically bound to both O_1 and O_1', being bound strongly to one and perhaps only weakly to the other. This would relieve the large deviation of H from the O_3 - O_1 line, and also would account for the uncertainty of the position of O_3 along y and z. There is no doubt, however, that the water is firmly held in the crystal - there was no evidence of disintegration at 150°C. The water performs a "space filling" rather than a "structure building" role.

Vibrations

There is significantly less vibration along x than along the other two directions. The isotropic 'B' values derived from B 11 and/

B 22 and B 33, are for Ni 2·46, 3·99 and 3·38 $Å^2$ respectively. The value for the light atoms are very variable and do not seem to have much physical meaning.

(h) Conclusions

The crystals of $Ni(histidine)_2.H_2O$ are composed of two kinds of complex: $Ni(D\ histidine)_2$ and $Ni(L\ histidine)_2$ related to each other by glide planes. Each histidine ligand is tridentate, and is co-ordinated to the nickel atom by the imidazole nitrogen(N_2) the "peptide" nitrogen (N_1) and a carboxyl oxygen(O_1). The bonds to Ni do not differ significantly in length, and agree with those quoted in literature. The co-ordination of Ni is very nearly regular octahedral. The two histidine ligands attached to Ni, are related by a two-fold axis passing through Ni, the two bulky imidazole rings being trans to one another, with O_1 and O_1' cis and also N_1 and N_1' cis. Comparison with the structures of the two zinc histidine complexes [3,4] and histidine hydrochloride [14] shows a significant difference in histidine conformation, brought about by rotation about the C_3-C_4 bond. Also the conformation along the N_1-C_2 bond is not staggered as in other determinations, and this is probably due to the stronger binding of O_1 and the fewer degrees of freedom in the nickel complex. The "peptide group" is not planar, the nitrogen deviating by about ·3 Å from the plane of the other atoms, as has been found elsewhere [4,14].

The crystal, which is very stable, is held together by an intricate system of hydrogen bonds, with Van der Waals' contact between parallel imidazole rings. The single water molecule does not hydrogen-bond in such a way as to help in binding molecules together, but seems to fill a vacant space in the crystal.

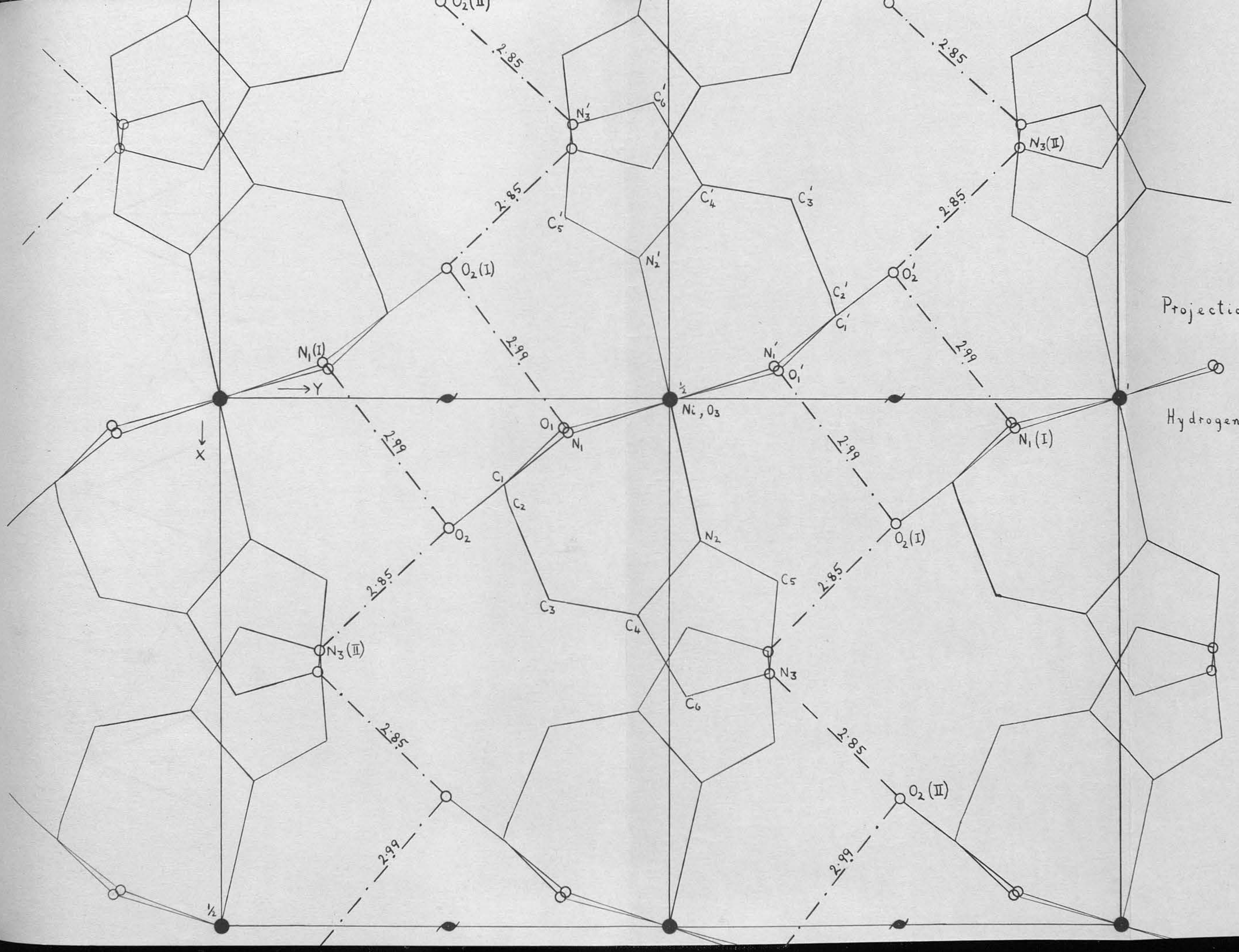


Fig 7

Projection along the c-axis

Hydrogen bonds: —·—·—

Fig. 8 Projection along the a-axis

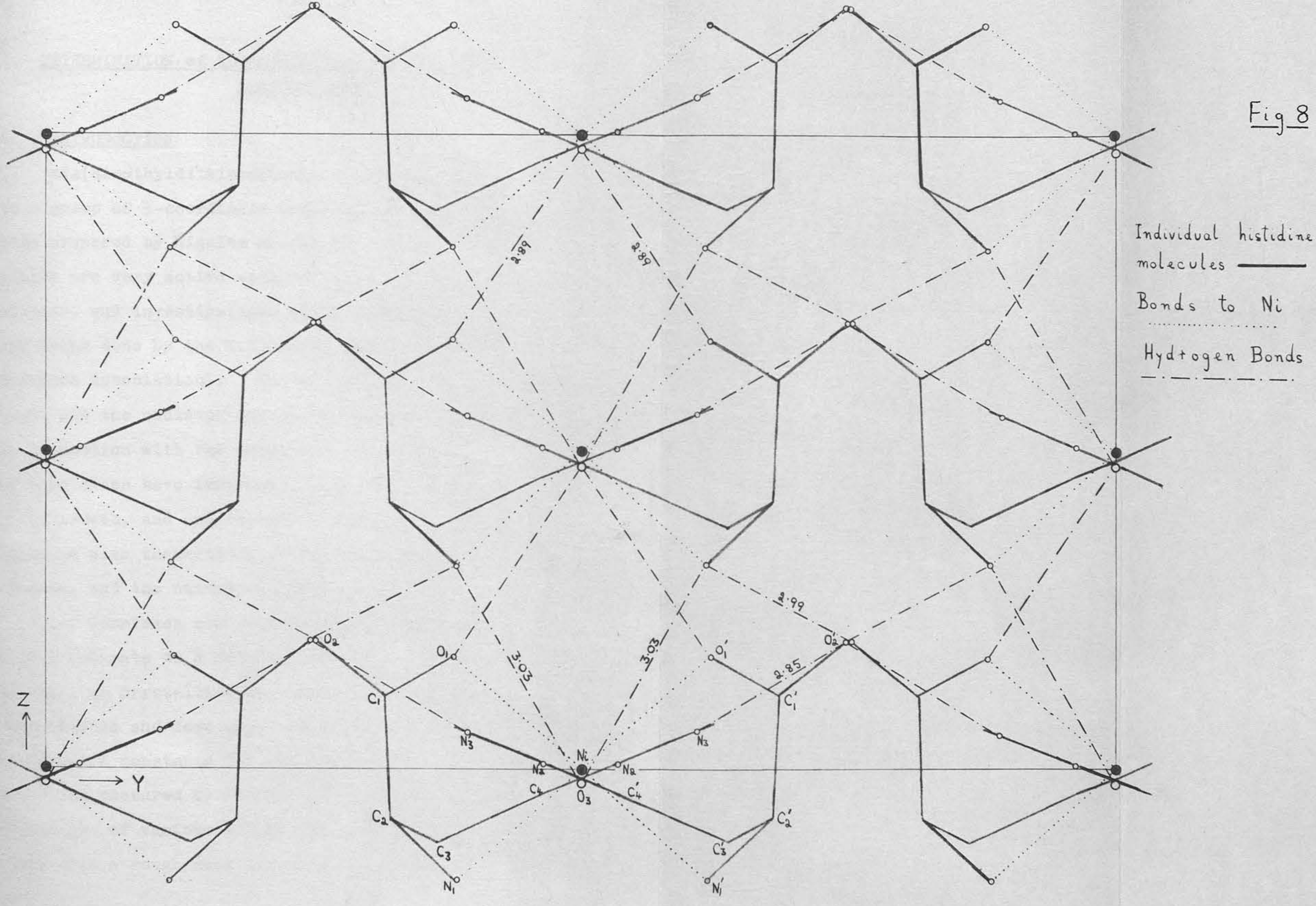


Fig 8

PART II

DETERMINATION of the STRUCTURE of BIS(DIMETHYLDITHIOCARBAMATO) PYRIDINE ZINC.

1. INTRODUCTION

Bis(dimethyldithiocarbamato) pyridine zinc, (PZDC), belongs to a group of 5-coordinate complexes of zinc, which have recently been prepared by Higgins and Saville [55]. Some of these complexes are very active accelerators of vulcanisation of rubber by sulphur, and investigations of the mechanism of vulcanisation [55] are being done by the N.R.P.R.A. (Natural Rubber Producers' Research Association). The effect of amine co-ordination on Zn-S bonds and the nucleophilic properties of the sulphurs, is important in connection with the details of acceleration. Certain derivatives of this class have important biological properties such as promoting plant growth, and are therefore important in agricultural problems. There is also theoretical interest in the unusual 5-coordinate state of zinc, and the nature of the N-C bond in dithiocarbamates.

1:1 Complexes are prepared by adding powdered zinc dialkyldithiocarbamate to a solution of the amine in warm benzene, and allowing to crystallise on cooling or evaporation. Most complexes are unstable and lose amine after a short exposure to air. The equilibrium constants for the dissociation of the 1:1 complexes have been measured by Saville [56]. Using this data, the relative affinities of various amines for the zinc can be compared. It is found that a rough sort of relation exists between amine basicity and/

amine affinity for zinc, but the steric effects of the nitrogen substituents seem to be quite important. For example, comparison of the pK_D (= $-\log_{10} K_D$) values for pyridine and methyl substituted pyridines, show that methyl groups in the 2 or 6 positions must be repelled by fields near the zinc or sulphur atoms:

		pK_D	Ref.
	pyridine	2·03	56
4-methyl	"	2·46	56
2-methyl	"	1·16	56
2,4,6-trimethyl	"	-·19	56

In comparison with the relation that exists for other amines between basicity and affinity for zinc, pyridine has an abnormally high affinity for zinc.

Zinc Co-ordination

The Zn^{++} ion has a completely filled 3d shell, and is therefore spherically symmetric. Its co-ordination geometry is therefore dominated by repulsions between bonding electron pairs, rather than repulsions between d-shell pairs and bonding pairs, as in most other transition metal complexes. 4-Coordinate Zn(II) complexes are common, and here the ligands take up tetrahedral positions that minimise repulsions between ligands. Typical examples are zinc blende, Zn S, and wurtzite, Zn O. For 6-coordination, the octahedral configuration minimises ligand electron pair repulsions, and all 6-coordinate Zn(II) complexes have this geometry. Some 6-coordinate Zn(II) complexes are described as having a tetragonal bipyramidal/

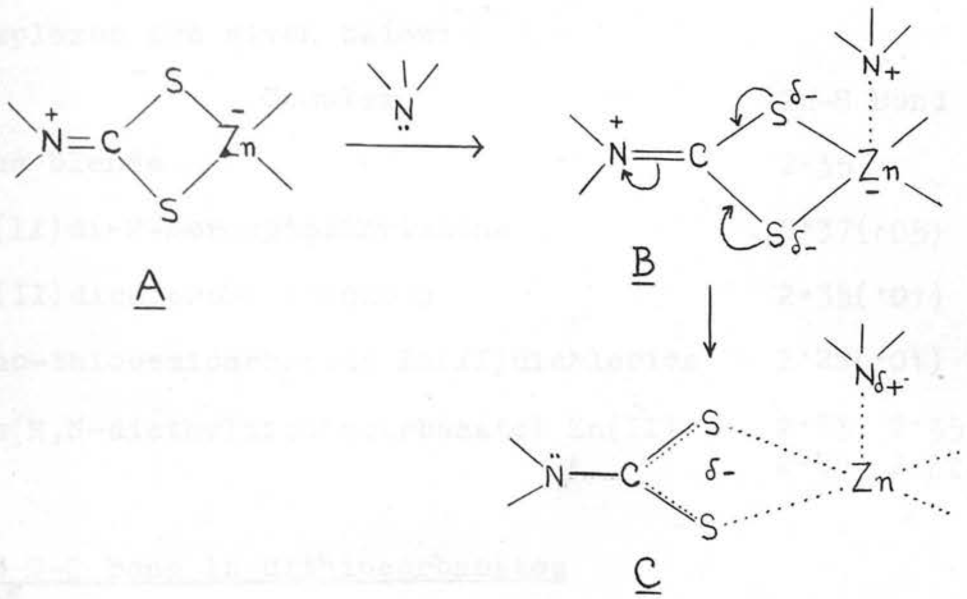
bipyramidal configuration (e.g. zinc 8-hydroxyquinolate dihydrate [57]), but this closely resembles the octahedral case and can be derived from it by extension of the two axial bonds.

Apart from complexes of the type (PZDC) discussed above, several examples of 5-coordinate Zn(II) are known [59,60,61,62,63] and the stereochemistry of 5-coordination has been reviewed by R.J. Gillespie [58]. The most favoured arrangement of 5 ligands is the trigonal bipyramid. In a molecule Zn X_5 of this symmetry, the axial electron pairs are subject to three repulsive forces from equatorial electron pairs at 90°. In contrast, the equatorial pairs have only two repulsions from axial pairs at 90°. In theory, therefore, the axial bonds should be slightly longer. This has been observed in zinc terpyridyl dichloride [59].

The other less probable 5-coordinate geometry is that of a square pyramid, based on an octahedral arrangement of electron pairs, one of which is a lone pair. Bis-salicylaldehyde ethylenedi-imine zinc monohydrate [62] has this configuration, and it is interesting to note that a trigonal bipyramidal arrangement would not be possible for this tetradentate ligand. The complexes bis(acetyl acetonato) zinc monohydrate [60,61] and bis(N,N-diethyldithiocarbamato) -Zn(II) [63], both have configurations intermediate between trigonal bipyramidal and square pyramidal. Both complexes have bidentate ligands which probably make the trigonal bipyramidal form less favourable.

Effect of amine co-ordination on Zn-S bonds

The infra-red investigations of Higgins and Saville [55], suggest that amine co-ordination to Zn increases the ionic character of the Zn-S bonds, and the sulphur 3p electron availability according to the scheme:



They attempted to justify this scheme by carrying out an experiment on the assumption that the increased electron availability would be accompanied by an increase in the sulphur nucleophilic properties. Diethyltrisulphide, $Et_2 S_3$, disproportionates into Et_2S_2 and higher poly-sulphides under the influence of a nucleophylic catalyst. Experiments were therefore carried out using as catalysts piperidine zinc dialkyldithiocarbamates, as well as piperidine and the parent zinc complexes alone. It was found that the rate constants are much greater for the amine complexes,/

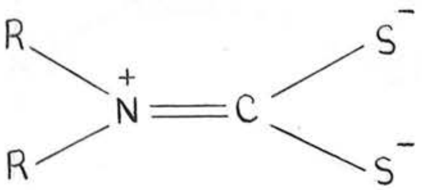
complexes, again suggesting that electron shifts similar to those outlined above, take place on amine co-ordination.

More direct evidence, however, is needed before this theory can be fully accepted. An increase in ionic character of the Zn-S bonds would almost certainly be accompanied by an increase in their length. Determinations of Zn-S bond length in various complexes are given below:

Complex	Zn-S Bond length	Ref.
Zinc blende	2·35	64
Zn(II)di-2-mercaptoethylamine	2·37(·05)	65
Zn(II)dichlorobisthiourea	2·35(·01)	66
mono-thiosemicarbazide Zn(II)dichloride	2·29(·01)	67
Bis(N,N-diethyldithiocarbamato) Zn(II)	2·33, 2·35, 2·38, 2·44, 2·82(·004)	63

The N-C bond in dithiocarbamates

Considerable theoretical interest is attached to the connection between the nature of the N-C bond and the biological activity of dithiocarbamates. Various derivatives of the type $R_2N\ C\ S_2.CH_2.COOH$ possess high and specific anti-fungal activity and promote plant growth. Their activity is maximum for $R{=}CH_3$ and decreases greatly when R is a higher alkyl. Kerk et al [68] have proposed that the activity depends on the occurrence of the structure:-



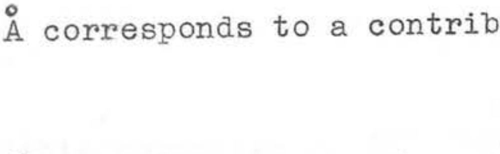
They/

They go on to propose that this structure may only be formed if N is aided by the alkyl groups in its mesomeric electron release to give a partial N-C double bond, and this effect should be a maximum for R = CH_3, and less for higher alkyls. In this way they explain the observed fall-off in biological activity.

Later evidence has cast serious doubt on this theory without giving an alternative explanation of the activity. Chatt et al [69] in an infra-red spectral study of Cu dialkyldithiocarbamates, found no difference in the N-C stretching frequencies when R was varied from methyl to propyl, and they concluded that the N-C bond order must be approximately constant over the series. Also X-Ray determinations of the N-C bond length show it to be quite constant in a variety of complexes.

Complex	N-C bond length (Å)	Ref.
Ni(II) diethyldithiocarbamate	1·33 (·015)	63
Cu(II) " "	1·35 (·017)	63
	1·35 (·017)	63
Zn(II) " "	1·33 (·019) av.	63
Cu(II) dipropyl "	1·33 (·05)	70
	1·33 (·05)	70

A length of 1·33 Å corresponds to a contribution of 84% of the form:-



The/

The effect of amine co-ordination to zinc on N-C bond order in the dithiocarbamate ligands, has been studied by Higgins and Saville [55]. They noticed significant shifts of N-C stretching absorption bands at 1500 cm^{-1} to lower frequencies on co-ordination, and reached the conclusion that the N-C bond order is reduced in the amine complexes. They qualified this by noting that various unassigned bands in the I.R. spectrum also shifted to lower frequencies on co-ordination. The electron shift scheme that they proposed to account for this reduction of N-C bond order, is the same as that which produces greater ionic character in the Zn-S bonds (see page 51). An X-Ray determination of N-C bond length in an amine complex is obviously required to settle this issue.

Crystallographic work on metal dithiocarbamates

(i) Bis(diethyldithiocarbamato) Zn(II) [63, 71]

Two independent determinations have been done, but that of Vaciago et al [63] is probably more accurate. The zinc is 5-coordinate with four short Zn-S bonds and one long Zn-S bond of 2·82 Å. The geometry is intermediate between a tetragonal pyramid and a trigonal bipyramid, and in the solid state it is a binuclear complex.

(ii) Bis(diethyldithiocarbamato) Cu(II) [63,71,72]

Three independent determinations have been made. It has the same structure as the corresponding zinc compound, the crystals being isomorphous.

(iii)/

(iii) Diethyldithiocarbamato Cu(I) [73]

The structure is built up of tetramers consisting of Cu_4 tetrahedra surrounded by four diethyldithiocarbamate molecules.

(iv) Bis(diethyldithiocarbamato) Ni(II) [63,74]

Two independent determinations have been made, but the results of Shugam et al [74] do not agree with those of Vaciago et al [63]. The latter are probably more accurate. The molecule is planar with Ni lying on a centre of symmetry.

(v) Bis(dipropyldithiocarbamato) Cu(II) [70]

A dimer with 5-coordinate Cu atom. There are four short Cu-S bonds and one long one, the structure being very similar to (i) and (ii) above.

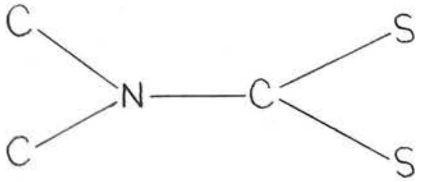
(vi) Bis(dimethyldithiocarbamato) nitroso Co(II) [75]

Co has a square pyramidal co-ordination, with the NO molecule forming an unsymmetrical π -complex with the Co atom.

(vii) Bis(hexamethylenedithiocarbamato) Cu(II) [71]

The Cu atom is 4-coordinate planar, and lies on a centre of symmetry.

In all these determinations the group



of the dithiocarbamate ligand is planar.

Objectives/

Objectives in the determination of the structure of (PZDC)

(i) To gather precise data about the 5-coordinate state of zinc. Only four other 5-coordinate zinc structures have been analysed.

(ii) To ascertain the effect of amine co-ordination on the Zn-S bonds and whether the latter are rendered more ionic according to the theories of Higgins and Saville [55].

(iii) To study the effect of amine co-ordination on the N-C bond. This is important in connection with the biological activity of these compounds [69, 68] and also in connection with the observations on N-C bond order made by Higgins and Saville [55].

(iv) To study the stereochemistry of the compound, and to see whether the stability of other amine zinc dithiocarbamate complexes can be explained in terms of steric repulsion.

2. INVESTIGATION OF BIS(DIMETHYLDITHIOCARBAMATO)PYRIDINE ZINC.

(a) Description of crystals

The crystals were prepared by Higgins and Saville [55] by adding powdered zinc dimethyldithiocarbamate (·02 moles) to a solution of pyridine (ca ·03 mole) in 20-40 ml of benzene, and crystallising by evaporation, cooling or adding light petroleum. The crystals were large clear plates, with a cleavage parallel to b, which decomposed slowly when exposed to air, losing pyridine. The equilibrium constant for this dissociation measured in toluene solution was $9·35 \times 10^{-3}$ [56]. As part of their proof that the crystals contained a 1:1 complex, Higgins and Saville determined the amount of zinc present. They observed 17·0% in the crystals, and the theoretical value for $C_5H_5N.\ Zn\ [S_2CN(CH_3)_2]_2$ is 17·0%.

(b) Unit cell and space group

By oscillation and Weissenberg photographs using a 5 cm. radius camera, the crystals were proved to be monoclinic. A value of b was found from a crystal set up about the b-axis, and values of a and c from a zero layer Weissenberg film calibrated by the shadow of knife edges at accurately known θ -values. β was as near to 90° as could be told by inspection of high order reflections. The results were:-

$a = 12·93\ (\pm ·03)$ Å

$b = 8·94\ (\pm ·09)$ Å

$c = 14·15\ (\pm ·03)$ Å

$\beta = 90°$

$V_c = 1636$ Å^3

The/

The density was determined by flotation in a KI solution using crystals fresh from their mother liquor:-

$$\rho_{obs} = 1{\cdot}535 \ (\pm {\cdot}001) \ g.cm^{-3}$$

The M.W. of the 1:1 complex is 384·9, and this together with V_c and ρ_{obs} gives Z = 3·93. Assuming Z = 4, the calculated density is 1·563 g.cm^{-3}. The rather low observed density may have been due to the partial loss of pyridine, but work proceeded on the assumption that there are 4 molecules in the unit cell.

A zero and 1st layer Weissenberg indicated the following conditions of reflections:-

h k l only for h + k = 2n

h o l only for h = 2n, l = 2n

These conditions fit space groups C 2/c (No. 15) and Cc. Both space groups have the additional condition that the o k o's are present only for k = 2n. This was not experimentally checked.

It is possible to fit 4 molecules into the unit cell in both space groups. In Cc (non-centrosymmetric) all atoms would have to lie on general (4-fold) positions. In C2/c (centrosymmetric) there are 8-fold general positions and 4-fold special positions on two-fold axes and centres of symmetry. Since the complex cannot have a centre of symmetry at Zn, it must lie on the two-fold axis if the space group is C 2/c; i.e. the two-fold axis must pass through Zn, N_1 and C_3 of pyridine.

No choice could be made between the two possible space groups at this stage.

(c)/

(c) Analysis of the b-axis projection

A crystal was rolled on fine emery paper to the shape of a cylinder parallel to the b-axis and the cleavage. It had diameter ·45 mm and was 1·7 mm long. It was coated in collodion to prevent decomposition. A series of zero layer intensity photographs were taken about the b-axis (5 cm. radius camera) with Cu Kα radiation. The intensities were measured by visual comparison with an intensity strip, and were LP corrected by hand. An absorption correction was applied, taking $\mu = 67{\cdot}6\ \text{cm}^{-1}$ and using the tables for cylinders given by W.L. Bond [44]. The data was rather limited and high orders were very weak. There were only four reflections measured with $\sin\theta > {\cdot}70$.

Unsharpened Patterson

This is shown in Fig. 9. In both C 2/c and Cc the unit cell translations are halved when projected down the b-axis. The unique area of the Patterson is therefore $\frac{1}{8}$th of the whole projected cell. It was originally hoped to be able to distinguish C 2/c and Cc using this Patterson. If the space group is C 2/c then only two unique Zn-S vectors should occur on the Patterson ; while in Cc there should formally be four. Of course there might easily be overlaps, and it might be difficult to distinguish four separate Zn-S peaks. In fact the Patterson shows only two peaks which could be Zn-S vectors and there is no visible splitting of either of them. Both are round and of good shape. This evidence strongly favours C 2/c (but does not prove it) and further work therefore proceeded on/

on this assumption.

Fourier Refinement

Structure factors were calculated with 5 atoms: Zn, N_1 and C_3 of pyridine at $0, \frac{1}{4}$; S_1 at ·032, ·431; S_2 at ·165, ·259. The sulphur positions were obtained from the Patterson. The R factor was 31.8%. The signs were used to phase a Fourier calculated with the observed F's. The result is shown in Fig. 10. It strongly resembles the Patterson synthesis, thus supporting its interpretation. There are peaks in reasonable positions and about the correct height for the light atoms of the molecule. The elongation of the ZnN_1C_3 peak in a direction between S_1 and S_2 was interpreted as C_1 and C_2 of pyridine. It is interesting to compare this fourier (see Fig. 10) with the final structure projected down its molecular two-fold axis (see Fig. 18). The peaks for some of the light atoms appear to be slightly off their expected positions, but no significance should be attached to this.

Three further rounds of Fourier refinement (S.F's followed by F_o-F_c maps) were done putting all the light atoms into the calculation. The agreement between F_o and F_c improved considerably (R fell from 31·8% → 26·9% → 22·6% → 20·0%). The difference maps indicated fairly small shifts in the S parameters, but the C and N shifts were very large and did not seem to make chemical sense in some cases. No great reliance was placed on them. The positions of C_6, C_7 and C_8 were especially doubtful. This lack of accuracy in light atom parameters was almost certainly due to the rather limited data available/

available which did not go out to the edge of the copper limiting circle.

The final co-ordinates (giving R = 20·0%) are given in Table 8, and a list of $|F_o|$ and $|F_c|$ in Appendix II.

(d) CONCLUSIONS

The doubt about the light atom positions in the Fourier refinement of the b-axis projection, showed that the data was not good enough to be able to locate them with sufficient accuracy. The analysis could have been carried into three dimensions, but there would still be inaccuracies in the light atom parameters due to the weakness or absence of the high order reflections. So attempts were made to recrystallise the complex. It was noticed at once that on recrystallising from a large excess of benzene, fine needles were obtained that gave good X-Ray photographs. The analysis of the b-axis projection was therefore abandoned.

Few conclusions of any interest can be drawn from this analysis itself. However comparison with the projection down the molecular two-fold axis of the complex (see Fig. 18) reveals some interesting points:-

(i) The b-axis Patterson and Fourier (Figs. 9 and 10) show quite a good agreement with the final structure, as determined in the crystals with benzene of crystallisation. The heavy atom positions agree well, but some of the light atom peaks, especially C_7 and C_8, are slightly off their expected positions. But there can be no doubt that in these crystals the molecular two-fold axis lies/

lies parallel or very nearly parallel to the b-axis. There is only one significant difference - the orientation of the pyridine ring. Both the Patterson and the Fourier indicate that the pyridine plane passes between S_1 and S_2, an orientation about 90° from that in the crystals with benzene of crystallisation.

(ii) The final analysis shows that the complex can probably possess exact two-fold symmetry in solution, although it does not in the crystals with benzene of crystallisation. It is very likely therefore that it will crystallise on a crystallographic two-fold axis whenever possible. This is strong evidence for C2/c as opposed to Cc. However it does not constitute proof. There is still the possibility, however unlikely, that the true space group is Cc. The two space groups are closely related. If objects of two-fold symmetry are placed in space group Cc with their axes parallel to b, the symmetry is transformed to that of C2/c. It is clear that if the objects are not exactly symmetric, the symmetry cannot be exactly C 2/c, although it must closely resemble it. Undoubtedly the symmetry of these crystals is very near to C 2/c, but this cannot be taken as proof that the complex possesses an accurate two-fold axis.

There does not seem to be any method capable of distinguishing the two space groups in a case like this. The statistical test of intensities would certainly indicate a centrosymmetric structure.

(iii) Packing.

The structure consists of sheets of molecules perpendicular to the/

the c-axis. One sheet is related to the next by the c glide, but due to lack of knowledge of the y co-ordinates, the interactions of one sheet with the next cannot be described in detail. However it can be said that their methyl groups are in contact, and one sheet "lies" on the methyl groups of its neighbour.

The packing within a sheet is of course face centred. The distance from C_3 of pyridine to Zn along y is 4.1 Å, and the pyridines therefore fit into the "pocket" of sulphur atoms of the molecule next along the y axis. Each pyridine probably has two contacts with methyl groups of C face-centred neighbours, one on either side. There are no pyridine-pyridine contacts as in the crystals with the benzene of crystallisation. This packing arrangement is consistent with the orientation of the pyridine ring.

Fig. 9 (010) Unsharpened Patterson.

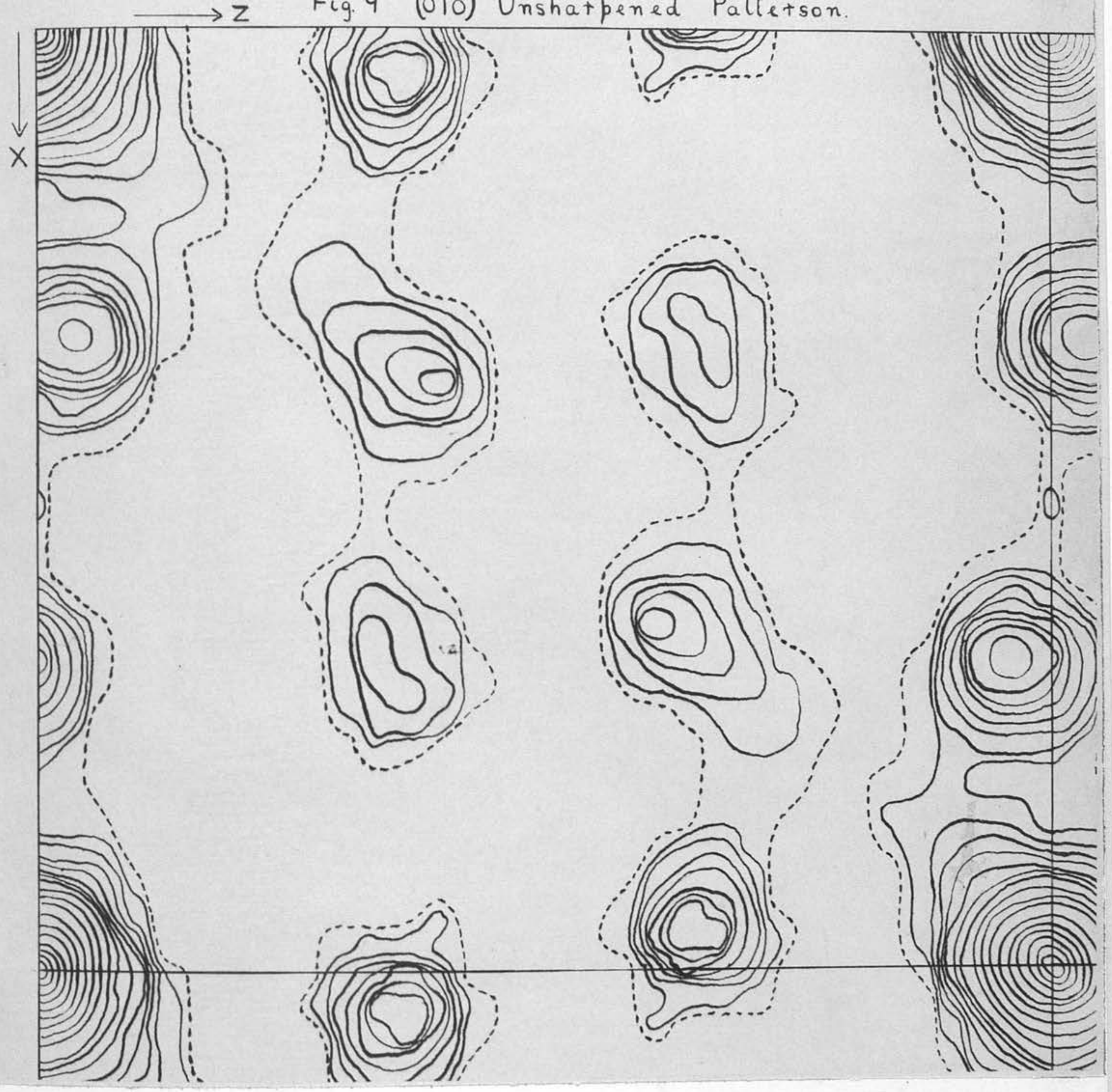
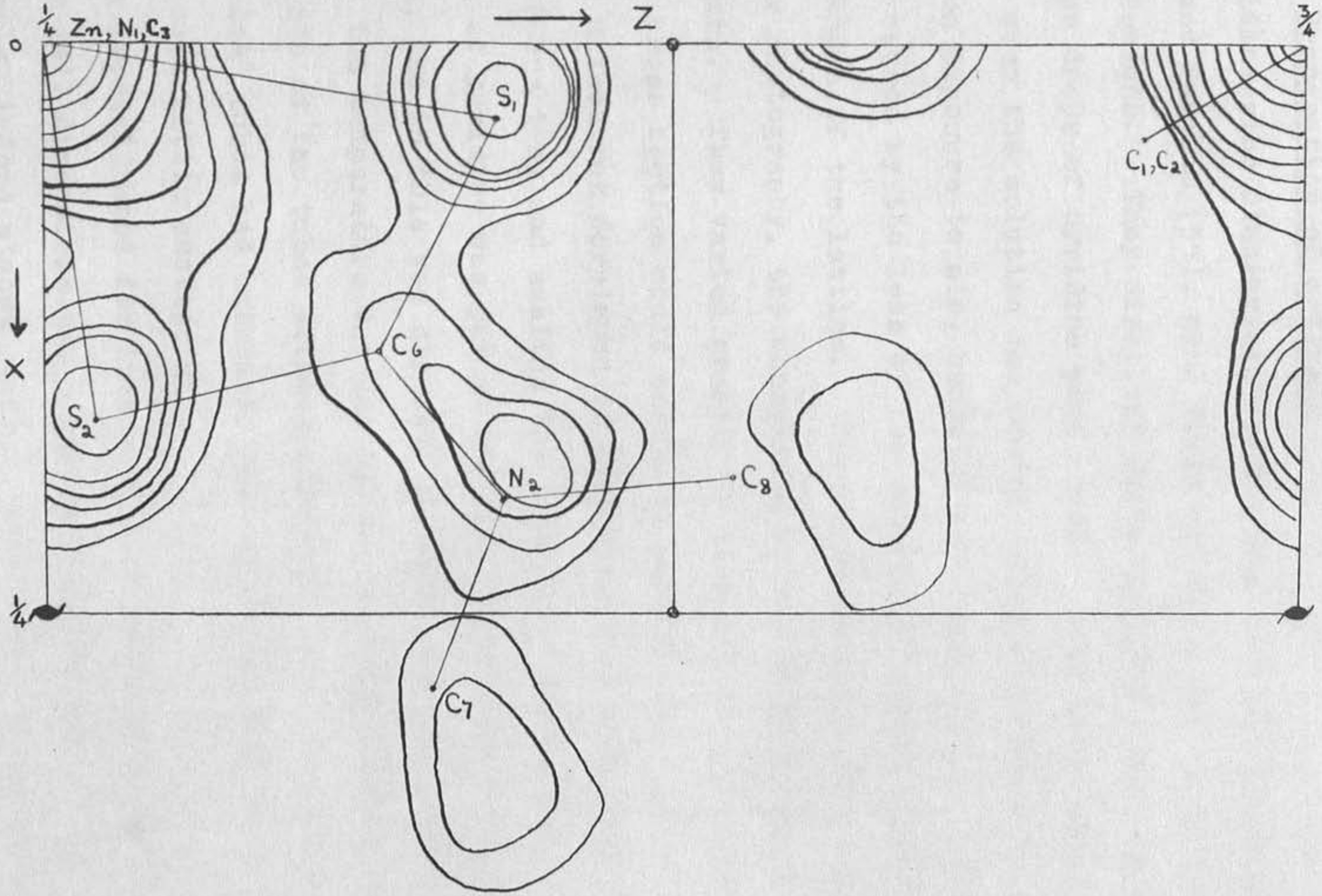


Fig. 10 (010) F_o Map



Positions found in final analysis given.
Contours at intervals of $1 e \mathring{A}^{-2}$ except on Zn, S_1, S_2.

3. DETERMINATION OF THE STRUCTURE OF BIS(DIMETHYLDITHIOCARBAMATO) PYRIDINE ZINC WITH BENZENE OF CRYSTALLISATION

(a) Preparation of crystals

Pyridine zinc dimethyldithiocarbamate crystals prepared by Higgins and Saville [55], were taken and dissolved in excess of boiling benzene. They dissolved quite easily but much more readily when a few drops of pyridine were added. Fine transparent needles appeared when the solution was cooled, which decomposed in a few minutes on exposure to air, becoming white and opaque. This was probably caused by the loss of the benzene of crystallisation and the breakdown of the lattice. The crystals had a very suitable shape for photography, the monoclinic b-axis being parallel to the needle axis. They varied greatly in size and small ones of suitable cross section could easily be picked out. After a few trials a method was developed of inserting them into "Pantak" tubes of diameter < 1 mm and sealing the tubes with picien wax. A small quantity of pyridine was put at one end of the tube away from the crystals, and in this way crystals could be kept for several weeks provided the temperature was not too high. The crystals adhered to the side of the tubes without adhesive, since they were so small. The "Pantak" tubes had extremely thin walls and photographs of them alone showed little scattering.

The crystal used for intensity work and determination of accurate cell dimensions was a needle 1·053 mm long. It had a very nearly, indeed almost perfect, cylindrical cross-section of diameter ·1442 mm. This was the result of equal development of numerous/

numerous [010] zone faces.

(b) Space Group

Equi-inclination Weissenberg photographs taken about the b-axis of layers 0-4, indicated only one condition of reflection:

h o l only for l = 2n.

This proved the presence of a c glide plane. The symmetry of the photographs proved the crystals to be monoclinic, and these facts limited the space group to one of: Pc, P2/c and $P2_1/c$. A zero layer Weissenberg taken about the [101] zone axis, however, showed another condition:

0 k 0 only for k = 2n.

This proved the presence of a two-fold screw axis parallel to b, and thus determined the space group to be $P2_1/c$.

Unit cell measurement

Accurate values of a^*, c^* and β^* were obtained from a zero layer Weissenberg taken about the b-axis with Cu K α radiation. The technique used was the same as that described on page 11. The calibration with copper wire lines on top and bottom of the film, gave a value of ·05008 cm/degree for the conversion factor. There were rather few reflections of sufficient intensity of the type h o o and o o l, but enough were found to give reasonable straight lines (see Figure 11).

The extrapolated values of a^* and c^* were:

$$\left.\begin{array}{lll} a^* = \cdot 12602 & \text{M.P.E.} = \pm \cdot 00008 \\ c^* = \cdot 07932 & \text{M.P.E.} = \pm \cdot 00008 \end{array}\right\} \text{Cu K}\alpha_1$$

An/

An accurate value of β^* was obtained from the $12.0.\overline{22}$ reflection whose sin θ = ·9929, and which was therefore particularly sensitive to changes in β^*. The cosine formula was used to derive an expression for sin θ and the experimentally determined values of a^* and c^* substituted.

cos β^* so obtained was ·2632 (± ·0013)

A value of b^* was measured from a zero layer Weissenberg taken about the [101] zone axis. One of the copper wire calibration plots is shown in Fig. 12 as an example. The extrapolation for b is shown in Fig. 11. There were only two reflections (0.8.0 and 0.10.0) available for accurate measurement, so a photograph was taken with white radiation and β spots were used as well. Also the reflections $1.9.\overline{1}$ and $2.10.\overline{2}$ whose sin θ values are not sensitive functions of a^*, c^* and β^*, were measured and used in the plot. The extrapolated value was:-

$b = 7{\cdot}966$ Å M.P.E. = ± ·004 Å

i.e. $b^* = {\cdot}1934$ M.P.E. = ± ·0001 (Cu $K\alpha_1$)

The final unit cell dimensions which were used throughout the rest of the work are given in Table 9.

Density

The density was measured by flotation in an aqueous solution of KI, using fresh crystals:

$$\rho_{obs} = 1{\cdot}422\ (\pm {\cdot}004)\ \text{g. cm}^{-3}$$

Assuming a cell contents of 4 molecules of the complex (M.W. = 384·9) and/

and 2 benzenes (M.W. = 78·1), the total "cell molecular weight" would be 1695·8. V_c, the measured cell volume, is 1961 Å³ and when combined with ρ_{obs} gives an observed "cell molecular weight" of 1679·5. The density calculated from the assumed cell contents and V_c is 1·436 g. cm^{-3}. The low value of ρ_{obs} was probably due to loss of benzene, and despite this small disagreement, work proceeded on the assumption of 4 molecules of the complex and two of benzene in the unit cell.

Two conclusions could then be drawn:

(i) The atoms of the complex must all lie on general equivalent positions.

(ii) The benzenes must lie on centres of symmetry.

Linear absorption co-efficient

The calculated value of μ for Cu Kα radiation (see page 15) is 57.0 cm^{-1}. More than two-thirds of this is due to the sulphur atoms.

(c) Collection of Data

Partial 3-dimensional data was collected from the crystal described on page 64, set up about the b-axis. The X-Ray tube, camera and film technique were exactly the same as that described on page 16. Equi-inclination photographs were taken of layers 0-4 using long exposures up to 50 hours and packs of 4 Industrial G films. The fourth layer had an inclination angle of μ = 23.0° and ξ = .78, so it would have been quite possible to continue photographs/

photographs up to layer 6 ($\mu = 35.8°$); but there already was a very large amount of data on layers 0-4.

The films were indexed quite easily by inspection, and the intensities measured using an intensity strip specially prepared from a strong reflection of suitable shape. Intensity measurement and inter-film scaling was done in exactly the same way as for $Ni(histidine)_2$.

Spot shape correction

(See page 18 for theory). Quite severe distortions of low ξ spots were present on layers 0-4, becoming worse on higher layers of course. This was attributed to the great length of the reflections coming from a crystal 1 mm long. If the extended intensities only had been measured, they could have been as much as 50% too low in some cases. Contracted and extended spots were therefore measured on either side of the film for a large selection of spots (30-50) on each layer. Ratios of It/Ie were obtained for each spot and plotted against ξ. The spread of the points was not large and fairly good curves could be judged. The curves for layers 1-4 are shown in Fig. 13 along with the spread of points in a typical case (layer 3). These curves were then used to correct Ie values, except for the selection of spots whose Ic values had also been measured. In these cases the mean of Ie and Ic was taken.

Absorption correction/

Absorption correction

Since the crystal used was an almost perfect cylinder, an accurate allowance for absorption could be made. The tables for cylinders given by W.L. Bond [44] were used with $\mu R = .406$ for the zero layer. The absorption correction factor, A^*, showed a maximum variation of 12% between $\theta = 0°$ and $\theta = 90°$ (see Fig. 13). This is certainly significant, and proves that it is well worth applying an absorption correction to the data. The curves for higher layers were obtained by using $\mu R \sec v$ (v = equi-inclination angle) instead of μR, and plotting against ξ instead of θ. The higher layer curves showed very little difference from the zero layer curve. The curve for each layer was combined directly with the spot shape curve for that layer (which was also plotted against ξ), and the function replotted against $\sin\theta$.

L.P. correction

All the data was L.P. corrected on Atlas using a program which was also capable of applying a modification function. Spot shape, absorption and L.P. correction were therefore all done in a single round of computation. At this stage each of the layers 0-4 was still on an arbitrary scale.

TABLE 9

SUMMARY OF DATA FOR

BIS(DIMETHYLDITHIOCARBAMATE) PYRIDINE ZINC. $\frac{1}{2}$ BENZENE

Space group: monoclinic $P\,2_1/c$

a = 12.670 (± .008) Å

b = 7.966 (± .004) Å

c = 20.134 (± .020) Å

β = 105.27° (± .06°)

Vc = 1961 $Å^3$.

Unit cell contents : 4 molecules of $C_{11}H_{17}S_4N_3Zn$

2 molecules of C_6H_6

Density observed = 1.422 $g.cm^{-3}$

Density calculated = 1.436 $g.\ cm^{-3}$

Linear absorption coefficient, μ = 57.0 cm^{-1}

Total unique observable reflections inside Cu limit = 4590 approx.

Total observed reflections (k = 0 to 4) = 2267

Total unobserved reflections (k = 0 to 4)

i.e. too weak to be observed = 444.

Fig 11

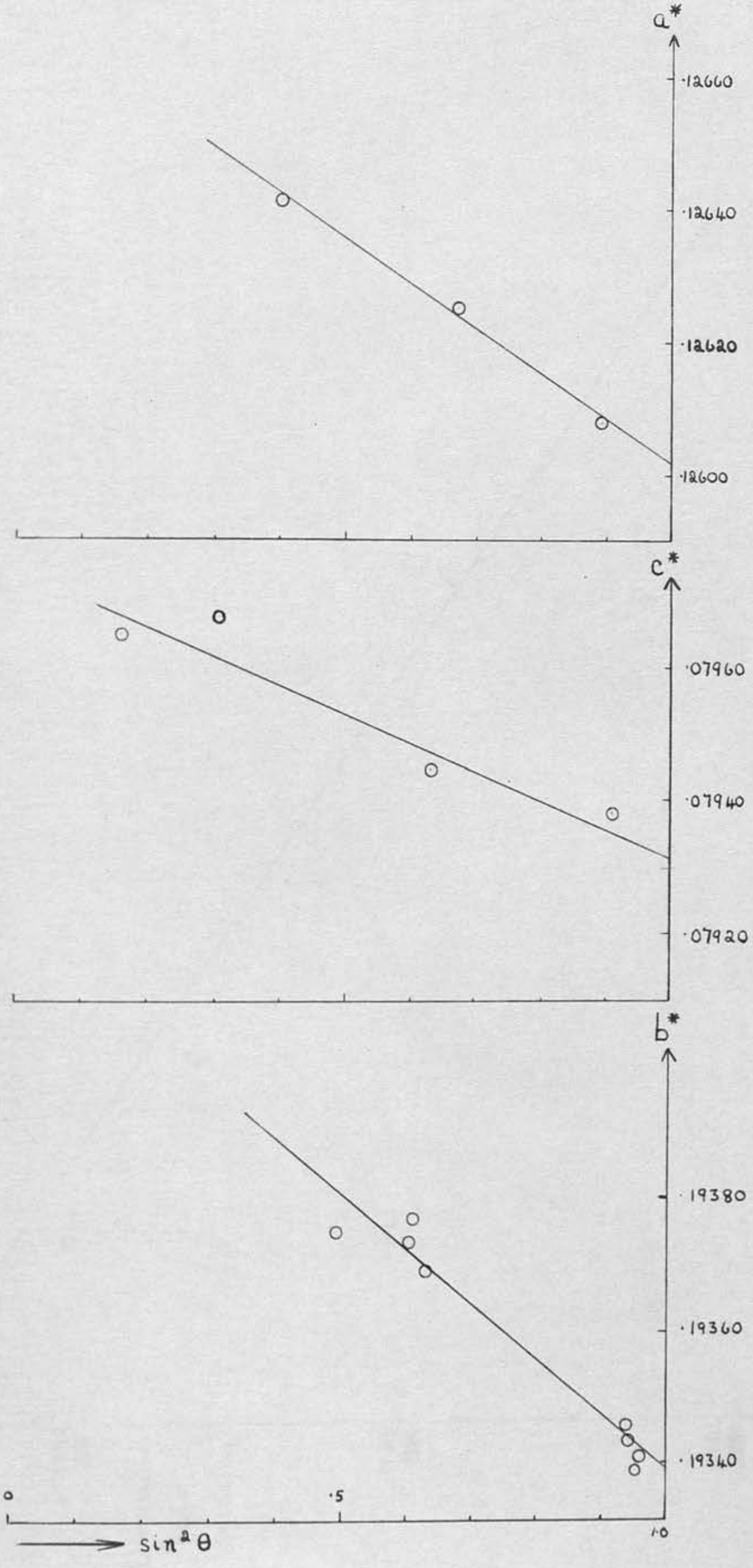

a*
·12660
·12640
·12620
·12600
c*
·07960
·07940
·07920
b*
·19380
·19360
·19340
0
·5
1·0
sin²θ

Fig 12

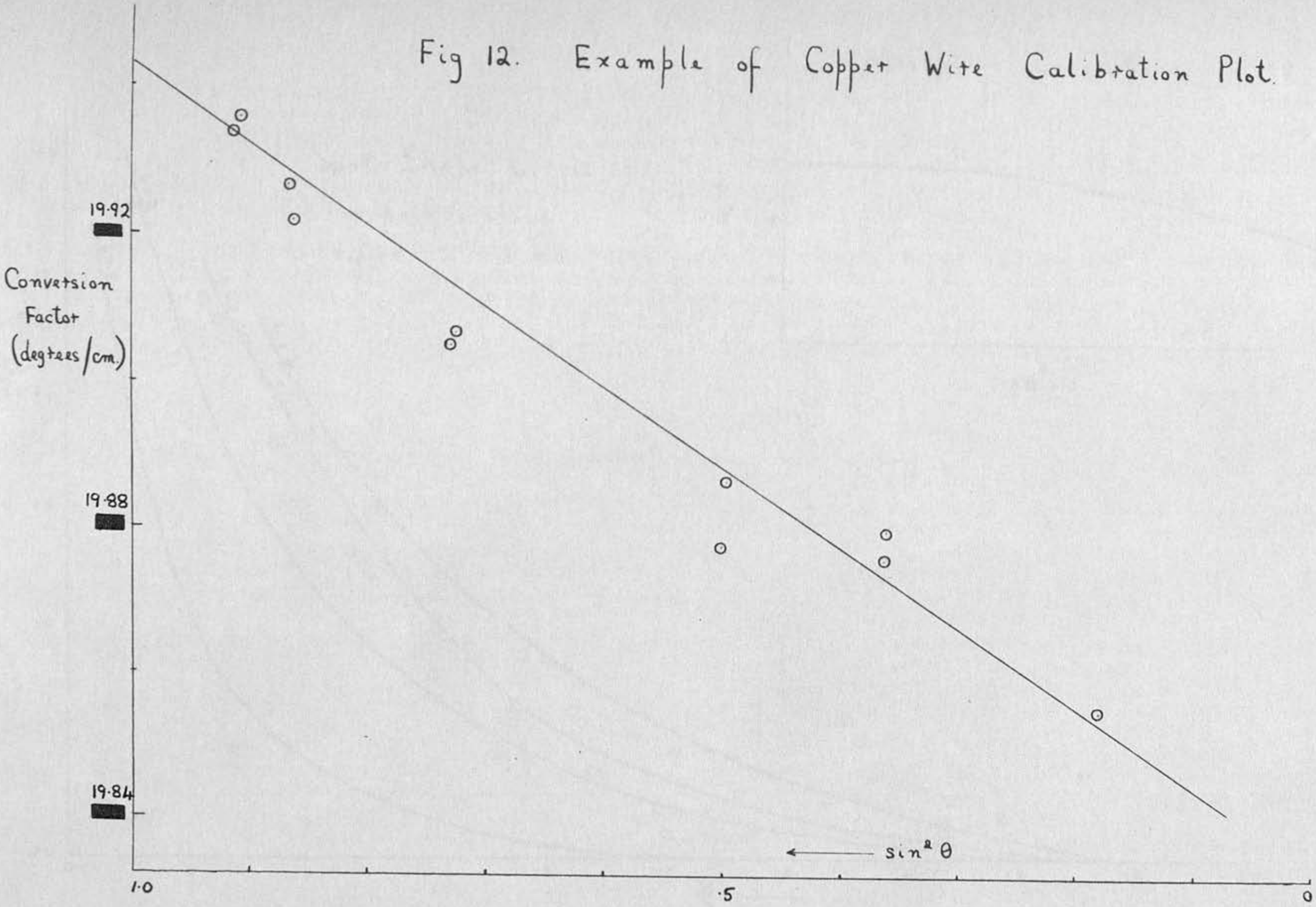


Fig 12. Example of Copper Wire Calibration Plot.

(d) Solving the structure

The general strategy was to determine the positions of the zinc and the 4 sulphur atoms in three dimensions, using the (010) and (101) projections. A three dimensional Fourier with observed F's and heavy atom phases, then showed all the light atoms clearly in reasonable positions. The structure is a fairly favourable one for application of the heavy atom method. $r(= \frac{\sum f_H^2}{\sum f_L^2}) = 1.67$. Now the percentage of structure factors having the same sign as F_H (the S.F. of the heavy atoms) is a function of r [45]. For r = 1.67 the percentage is about 88%. With this fairly high percentage of correctly signed structure factors, it is not surprising that the Fourier phased on the heavy atoms, showed the light atoms with quite good resolution.

(i) (010) Projection

The projection down the y-axis (b = 7.966 Å) was a very favourable one with few overlapping atoms. The only bad overlaps were C_9 and S_4, N_3 and C_{11}. The zinc and sulphur positions were found initially from a sharpened Patterson and then refined by Fourier methods.

Patterson Function

Both sharpened and unsharpened Patterson projections were calculated. The sharpening function was calculated by averaging F^2 values over ranges of $\sin^2\theta$ and plotting the mean, $\langle F^2 \rangle$ against $\langle \sin\theta \rangle$, and then choosing a function so as to make this curve a straight line parallel to the $\langle \sin\theta \rangle$, axis; i.e. sharpening/

sharpening to point atoms. The two Pattersons were very different, the unsharpened one showing very large smooth peaks and no detail, while the sharpened one had very sharp narrow peaks many of which did not appear at all on the unsharpened version. The rather extreme sharpening function produced a few spurious peaks which were recognised as such later on. The largest vector peak, apart from the origin, present on both versions, was 2.4 Å from the origin and was rather distorted. This was very unlikely to be the Zn-Zn vector because the packing along the b-axis would not allow it. The next largest vector, still about twice the weight of any other vector, at a distance of 6.8 Å from the origin, was therefore taken to be the Zn-Zn vector. A superposition on this peak then gave reasonable sulphur positions (almost the correct ones). At this stage the ideas gained about the structure from the first analysis were very helpful. The large distorted peak at 2.4 Å was explained as two superimposed Zn-S vectors. Possible peaks for the pyridine were noticed but they were not very well defined. From the positions of the sulphur atom, the pyridine axis had to lie roughly in the plane of projection.

Structure factors and F_o map

Before structure factors could be calculated, the temperature factors of the atoms had to be estimated. A Wilson plot (see Fig. 14) gave an overall value, $B = 3.0$ Å^2 which was given to zinc and the four sulphur atoms in the positions determined from the Patterson/

Patterson. The agreement shown between F_o and F_c was fair, high values of F_o being matched for the most part by high F_c. R = 45.9%.

Before computing the F_o Fourier, those large F_o values whose signs were doubtful (i.e. whose F_c values were low) were eliminated from the list. The Peaks for Zn and S atoms were approximately the correct height and small shifts of about .1 Å were indicated. Booth's method [47] was used to find the maxima. Peaks of about 2-3 ε's Å^{-3}* were in the expected position of pyridine, indicating the ring to lie at a small angle to the plane of projection, but C_3 and C_4 peaks came up rather far away from their true positions. C_6 and N_2 had peaks of 2 ε's Å^{-3} but C_7 and C_8 did not come up well. C_9, C_{11}, N_3 and S_4 were all coalesced into one large distorted peak, and there was rather a misleading spurious peak about .5 Å from C_{11}. C_{10} had a good peak of 2 ε's Å^{-3}. The benzene molecule was quite well resolved with peaks of 2-3 ε's Å^{-3}, but as might be expected there was a spurious peak on the centre of symmetry. Of the light atoms, the pyridine positions were the most reliable, and C_6 and C_9 could be fixed by the positions of the sulphur atoms, and so these were used to phase a second round of structure factors followed by a F_o-F_c map.

Structure factors and F_o-F_c Map

Structure factors were computed putting Zn, S_{1-4}, the atoms of pyridine, C_6 and C_9 in the positions determined from the F_o map. All were given B = 3.0 Å^2. R = 36.8%. The F_o-F_c map was computed eliminating all large F_o values whose signs were doubtful. A

shift/

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* For " ε's Å^{-3} " read " e.Å^{-3} " (and hereafter)

shift of .05 Å was indicated for Zn, .06 Å for S_2, .04 Å for S_4, and smaller shifts for S_1 and S_3. Shifts for the pyridine atoms varied from Zero (N_1) to .25 Å (C_1). Except for N_3, C_{10} and C_7, positive peaks corresponding to atoms not put into the S.F. calculation were rather poor. However taking the evidence of this difference map and the preceding F_o map, reasonable positions were inferred for all atoms except C_{11}.

Structure factors and F_o map (see Fig. 15)

All atoms except C_{11} were included in this calculation, all 'B' values again being taken at 3.0 Å^2. R = 22.7%. The F_o map calculated using all the terms is shown in Fig. 15. All atoms appear with separate maxima except C_9 on the S_4 peak and C_{11} on the N_3 peak. The peaks are all about the correct height but some of the light atom peaks are rather distorted, especially C_5 which lies rather close to the two-fold screw axis. The benzene peaks around the centre of symmetry indicate the benzene ring to lie at a small angle to the plane of projection. The Fourier clearly shows the large unoccupied region surrounding the benzene.

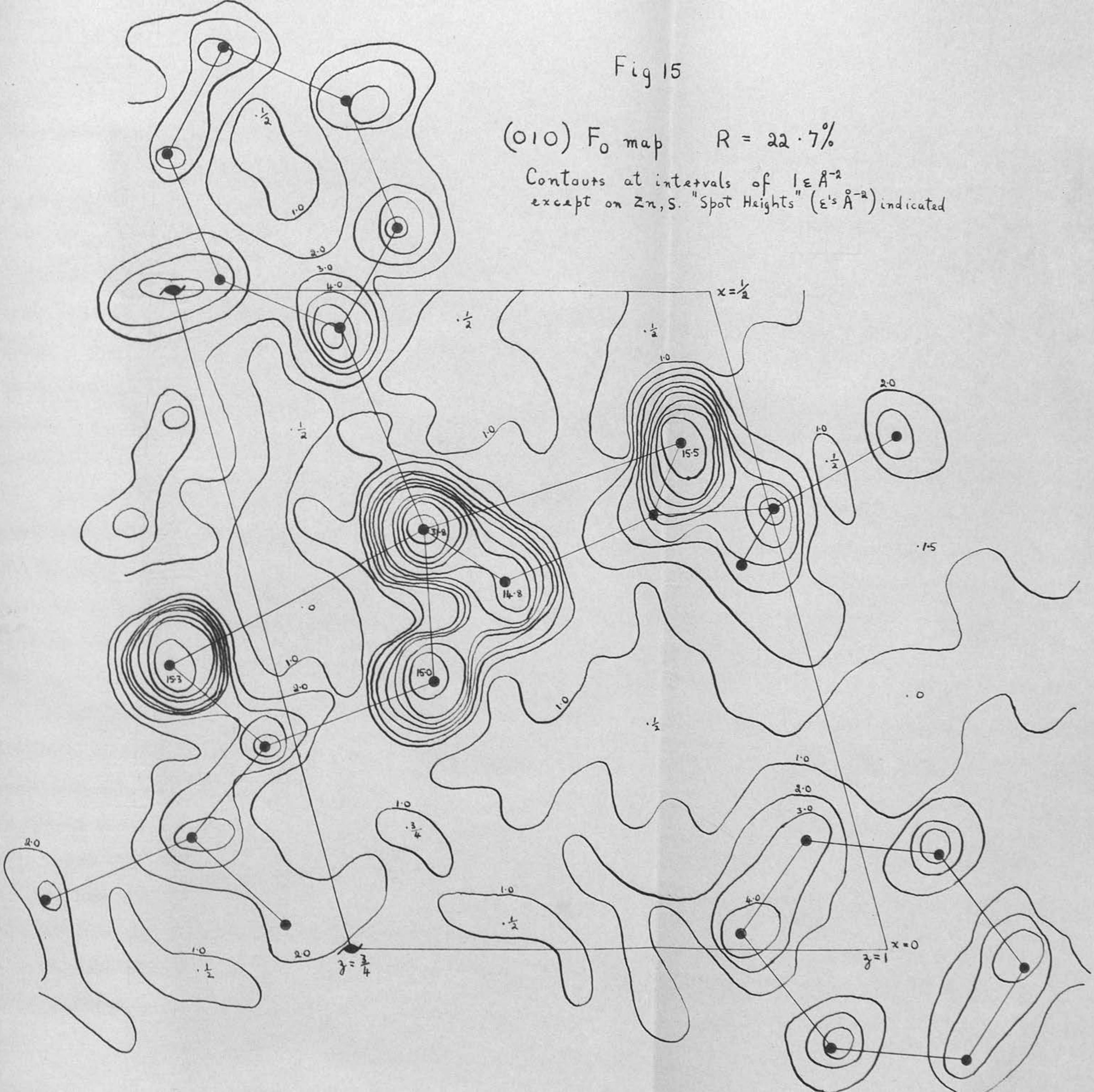
Conclusions from the (010) analysis

The evidence of the R factor (= 22.7%) and F_o map proved beyond doubt that the zinc and sulphur positions were correct. Their refined x and z parameters were later used to phase a 3-D F_o map. Although the x and z parameters of most of the light atoms were also known at least approximately, they were never used again/

Fig 15

(010) F_0 map $R = 22 \cdot 7\%$

Contours at intervals of $1\,\varepsilon\,\text{Å}^{-2}$ except on Zn, S. "Spot Heights" (ε's Å^{-2}) indicated



again in later refinement. This surplus information was, however, very helpful in interpreting the 3-D F_o map.

(ii) (101) Projection

With some difficulty a crystal fragment was sealed in a "Pantax" tube and orientated about the [101] zone axis, giving a very long projection of about 20.6 Å along the long diagonal of the cell. The dimensions of the projected cell were 7.966 Å x 11.85 Å. It is not surprising that little success was achieved with this projection, and recourse had to be made to a generalised (010) Patterson projection to settle the y parameters of the heavy atoms.

The crystal had a very irregular shape, but was roughly spherical with a diameter ranging from .28 to .20 mm. Absorption was therefore quite large and difficult to estimate, and no great reliance could be placed in the intensities. None of them were used in the final refinement, and there were too few (~100) to give good inter-laying scaling.

A Patterson, sharpened to point atoms, was first computed. The symmetry of the projection was pgg and so the symmetry of the Patterson was pmm. From the x and z parameters a Zn-Zn vector had to lie on a line parallel to y and distant .5 Å from y. There were only three possibilities:- (i) on the edge of the origin peak, (ii) on the edge of a very weak peak at y = .3 and (iii) on a weak peak at y = .5. None of these was very convincing.

To help with the interpretation of the Patterson a generalised (010) Patterson projection was computed with k = 1 data. The data was/

was unsharpened. It was compared with the (010) unsharpened Patterson and the relative y parameters of the Zn and sulphur atoms calculated. Zn, S_1 and S_4 were found to have roughly the same y parameters.

The Zn y parameter indicated the weak peak at y = .3 on the (101) Patterson projection to be the Zn-Zn vector. A very large peak at about $(.27, \frac{1}{2})$ agreed with this interpretation, the peak being a Zn-Zn vector between c glide related molecules. Another very large distorted peak at $(\frac{1}{2}, \frac{1}{2})$ was in the expected position for the remaining Zn-Zn and Zn-S vectors. A superposition done on the peak at $(.27, \frac{1}{2})$ indicated some reasonable sulphur y parameters that were in rough agreement with those derived from the generalised (010) projection. It was difficult to fix the sulphur y parameters to within .3 Å and S_1, Zn and S_4 overlapped rather badly.

The y parameters of the zinc and sulphurs were next refined by two rounds of structure factors followed by F_o-F_c maps. No shifts were made in the x and z parameters which were more accurately determined from the (010) projection. In the first round the shifts calculated were:-

Zn .04 Å; S_1, S_2, S_3 about .08 Å and S_4 .14 Å .

The second round shifts were much smaller - about .03 Å on average - indicating the parameters to have settled down. The (101) data was not good enough to be able to detect any light atoms on the difference maps.

The very weak, practically absent, Zn-Zn vector of the Patterson/

Patterson was probably due to the rather severe sharpening function used, and perhaps also absorption in the crystal.

Zinc and Sulphur positions from the (010) and (101) projections

	x/a	y/b	z/c
Zn	.3195	.6655	.3342
S_1	.2147	.6698	.2010
S_2	.2047	.4203	.3202
S_3	.2778	.9347	.3647
S_4	.3867	.6888	.4678

(iii) 3-D F_o Map phased on zinc and sulphurs

Before structure factors could be calculated, more accurate temperature factors were obtained for each layer by doing Wilson plots [76]. $\text{Log}_{10} \dfrac{\langle I \rangle}{\langle f_o^2 \rangle}$ values were calculated over ranges of .1 in $\sin^2 \theta$ and the values plotted against $\sin^2 \theta$. Fairly good straight lines were obtained (see Fig. 14). The 'B' values calculated from the gradients were 3.05 Å^2 (k = 0), 3.76 Å^2 (k = 1), 3.20 Å^2 (k = 2) and 4.44 Å^2 (k = 3). These values are similar to the final isotropic B values for the heavy atoms.

No suitable program was available to calculate structure factors for $P2_1/c$, so a program was written in Atlas Autocode to do this, and scale the layers separately to F_c, taking the scale factor to be $\dfrac{\sum |F_c|}{\sum |F_o|}$ (Fraser Program 2/5, see page 98). Structure factors were then calculated putting the Zn and four S atoms in the positions/

positions given above, giving to each atom the overall B value determined for each layer. The data input to the computer was on a scale determined for each layer from the intercept of the Wilson plots. The scale factors evaluated on scaling to F_c were 2.60, 1.63, 1.72 and 2.10 for layers 0 to 3 respectively.

The Wilson plots therefore greatly underestimated the true scale of the data. These scale factors themselves were an underestimate since only the heavy atoms were included in F_c. The overall value of R was 39.6% and varied from 35.9% for k = 0 data to 42.1% for k = 4 data.

The signs of this calculation were used to calculate a 3-D F_o map on Atlas using Harding program 7/2. All large F_o values whose signs were doubtful were omitted. Sixteen sections were taken at intervals of c/60 from $z = 0 - \frac{1}{4}$, and values were computed at intervals of a/60 along z (0 - 1) and b/15 along y (0 - 1). The line printer output sheets were contoured directly although there was some distortion.

All atoms, except hydrogens, appeared with fairly reasonable electron densities in their expected positions. The peak electron densities ($\mathcal{E}$'s $\mathring{A}^{-3}$) by interpolation were:-

Zn 40.5, S from 21.1 to 22.9, N from 5.2 (N_2) to 5.4 (N_1) and C ranging from 2.5 (C_8) to 4.9 (C_6). The positions of maximum peak density were determined using Booth's method [47] and a correction applied to x/a and z/c parameters to allow for the skewness of the axes. The x/a and z/c parameters of the light atoms so derived were certainly better than those of the (010) projection./

projection.

For the heavy atoms, however, it was doubtful which were more accurate, and so the two sets of values were averaged. The refined y/b values from the (101) projection were certainly more accurate than those from the 3-D F_o map (the interval of evaluation along y was b/15 = .53 Å, giving rather a large interpolation). Finally revised 'B' values were estimated for each atom taking into account the peak height and the probability of high or low vibration at its position in the molecule.

As a check on whether these positions made chemical sense or not, bond lengths and angles were calculated. All atoms seemed to be in reasonable positions, although some bond lengths (e.g. in pyridine and benzene) differed by nearly .2 Å from the theoretical values. However no attempt was made at this stage or at any time in the refinement, to alter the co-ordinates to make them fit the expected structure. It is very likely that if a compromise had been used between the calculated and expected co-ordinates, the convergence to the final parameters might have been quicker, and fewer rounds of least squares would have been required.

Structure factors and 3-D F_o-F_c map.

The co-ordinates and 'B' values of all 22 unique atoms were used to calculate structure factors using Fraser program 2/5, scaling each layer separately to F_c. The overall R factor was 19.7% (omitting unobserved reflections) and the R factors for layers 0-4 were respectively: 15.3, 15.6, 19.4, 23.4, 27.3. These values reflect/

reflect the expected rise in R with θ (a greater proportion of high θ spots on upper layers) and also the greater errors in the intensities due to spot shapes on upper layers. Increases in scale factor (applied to F_o) for each of the layers 0-4 were respectively 1.2%, 14.7%, 6.4%, 11.0% and 5.6%.

The signs of this calculation (all terms included) were used to calculate a 3-D F_o-F_c map in exactly the same way as the 3-D F_o map. This showed a background electron density of between $\pm$ .5 $\mathcal{E}$'s Å^{-3}, with some larger positive and negative areas near the heavy atoms. Gradients were measured at each atom along the three axial directions and shifts computed as given on page 31. Values of p were obtained from the F_o map by plotting log ρ against r^2 (ρ = electron density at distance r from atomic centre) in a number of typical cases, for Zn $p = 6.2$ Å^{-2}, for S , 4.7 to 6.3, for C , 4.3 to 6.6, for N , 7.4. The shifts were Zn .009 Å , S_1 .045 Å, S_2 .015 Å, S_3 zero, S_4 .019 Å, and light atoms an average of .015 Å in the xz plane and .03 Å in the y direction. The largest shift was .18 Å for C_8. The 'B' values of each atom were revised by taking the value of Δ at each atom, and relating this to a set of theoretical f curves for each atom at different 'B' values.

The effect of making these shifts was to produce a fall in R from 19.7% to 17.2%.

(e) Least squares refinement

The process of seven rounds of least squares refinement which produced convergence, is summarised in Table 10. The f curves used were as follows:-

Zn (atom) anomalous dispersion corrected - Dauben [77]
S (atom) " " " - Vaciago [78]
N No anomolous dispersion correction - Hoetni and Ibets ~~Freeman~~ [51]
C " " " " - Berghuis [52]
H " " " " - McWeeny [79].

Throughout all rounds, F_o terms too weak to be observed were omitted. The first three rounds were done on Mercury using a program written by J.S. Rollett (see page 97). The weighting scheme (No. 1) used, took w as a function of F_o such that $w = |F_o| / F^*$. if $|F_o| < F^*$ and otherwise $w = F^* / |F_o|$. F^* was taken at $.14\, F_o^{MAX.}$, so that very large F_o terms had weights approaching .14, and very low F_o terms had correspondingly low weights. The temperature factors were kept isotropic and no hydrogens were included. The small drop in R from 17.2% to 17.0% produced by the first round was caused by the scale factor, k, input to the first round that was 12.6% too high. This error in k was mostly caused by scaling to F_c using $\Sigma F_c / \Sigma F_o$, when the F_o list contained a large number of zeros, but also in part by underestimated temperature factors. The first round produced a large negative shift in k, and the second round large positive shifts in B for all atoms averaging + .8 Å^2. These corrections were mostly responsible for the/

the large drop in R from 17.0% to 12.73% produced by Round 2.

Refinement was stopped temporarily after Round 3 in order to improve the relative scaling of the layers. At the same time it was convenient to put the data on magnetic tape. A modified version of Fraser program 2/5 was written which would transfer data to magnetic tape, and this was run on Atlas at N.I.R.N.S., Harwell. Previously the layers had been scaled to F_c just before the 3-D F_o-F_c map. The scale factors relative to those were: .897, .889, .890, .860, .866 for layers 0-4 respectively.

The last four rounds were computed with a program, SFLS DIAMAND /MMH (see page 97) which was very similar to that of J.S. Rollett. The weighting scheme (No. 2) was now $\sqrt{w} = F^{*}/|F_o|$ if $|F_o| > F^{*}$ and $\sqrt{w} = 1$ otherwise. F^{*} was taken at .28 F_o max. Those hydrogen atoms which were fixed by the carbons (i.e. hydrogens of pyridine and benzene) were put into the calculation, and the heavy atoms were allowed to become anisotropic. The effect of putting in the 8 hydrogens atoms (which produced $\Delta R = -2.8\%$ later on), and the further refinement of parameters in Round 3 produced the comparatively small fall of .43% in R. This was probably caused by the 1% overestimate of k when scaling to F_c after Round 3. The overestimate in turn was probably due to the large effect of extinction when using $k = \sum F_c / \sum F_o$. $k = \left(\sum F_o / F_c\right) / n$ would have produced better results. In Round 5 all atoms except C_7, C_8, C_{10} and C_{11} of the methyl groups and hydrogens were given anisotropic vibrations. The methyl carbons were kept isotropic in case their vibrational/

Note:

The vibration parameters in the structure factor calculation leading to the 3-D ($F_o - F_c$) electron density map, were incorrectly treated. This should be borne in mind when studying the discussion given on pages 82 - 83. It accounts for the rather unusual features near the heavy atoms (see Fig. 16), and the high value of R.

vibrational ellipsoids became elongated in the direction of their hydrogens. The very small drop in R and $\sum w \Delta^2$ produced by Round 6 indicated convergence. Estimated standard deviations (E.S.D.'s) of the co-ordinates were obtained in each round from the diagonal element of the matrix. Due to the block diagonal approximation the E.S.D.'s were probably slightly underestimated. The ratio of ~~E.S.D./shift~~ shift : E.S.D. produced by Round 7 was about .2 to .3 for most atoms and only in the case of four co-ordinates did it exceed .5 . The maximum ratio was .63 for C_7. Although the E.S.D.'s of atoms varied widely the percentage fall in E.S.D. for all atoms except Zn, was quite constant from one round to the next. Taking the E.S.D.'s produced by Round 7 to be unity, E.S.D.'s of Rounds 5 and 6 were as follows:-

	Round 5	Round 6	Round 7
Zn	1.13	1.01	1.00
all other atoms	1.62	1.42	1.00

These ratios were remarkably constant for sulphur and the light atoms and for all three co-ordinates. They show that there was a quite considerable increase in accuracy of the parameters in the last round.

3-D F_o-F_c map (see note opposite)

A final difference map was calculated leaving out all the hydrogen contributions to F_c, in order to detect the hydrogens of the methyl groups. Harding program 7/8 which was able to accept anisotropic temperature factors, was used and the parameters were

the/

the output of Round 7. The R factor was 10.8%. This rise of 2.8% in R may be taken as a measure of the contribution of the eight hydrogens to R.

The eight hydrogens whose positions were accurately known, all appeared on positive areas (see Fig. 16), but in many cases the peak density was slightly off the expected position, the worst case being H_{12} which was .25 Å away from its calculated position. H_3 had a very good roughly spherical peak of P.D. (peak density) .82 ε's $Å^{-3}$. H_1, H_4, H_5, H_{12} and H_{13} all had rather large, somewhat diffuse peaks of P.D. .4 to .6 ε's $Å^{-3}$. H_{11} had the poorest peak of P.D. .35 ε's $Å^{-3}$. A brief search was made for the twelve methyl hydrogens and there were rather large areas of low positive electron density (.2 to .4 ε's $Å^{-3}$) in the expected regions. The methyl hydrogens are probably subject to greater vibration that those of pyridine and benzene, and the methyl carbons had on average larger temperature factors than the ring carbons. This and the fact that they were left out of least squares refinement, produced poor resolution on the difference map. Although no methyl hydrogen positions were determined, they could probably have been found by projecting the electron density down the $N-CH_3$ bonds and looking for trigonal symmetry. Considering that 8 hydrogens produced a $\Delta R = -2.8\%$, the inclusion of another 12 hydrogens (equivalent to two carbon atoms in electrons) might well have produced a much better value of R.

The features on the difference map at Zn, S_3 and S_4 are shown in Fig. 16. Similar features occurred at S_1 and S_2.

TABLE 10

SUMMARY OF SOLUTION AND REFINEMENT OF STRUCTURE.

(010) projection

Patterson
↓
Fourier refinement R = 22.7%
↓
Refined x/a and z/c parameters
for Zn and 4 sulphurs

(101) projection

Patterson
↓
Generalised (010) Patterson
↓
Fourier refinement
↓
Refined y/b parameters
for Zn and 4 sulphurs

3-D F_o map phased on Zn and 4 sulphurs R = 39.6%
↓
3-D (F_o-F_c) map with all atoms included R = 19.7%
↓
3-D least squares refinement

Round	Hydrogens	Temperature Factors	Weights	k Scale factor applied to Fo	$\sum\omega\Delta^2 x10^{-5}$	R%
	None	All isotropic	1	1.0000	645	17.2
1						
	None	" "	1	.8740	392	17.0
2						
	None	" "	1	.8800	214	12.73
3				.8720	-	-
	8 H atoms	Zn, S_{1-4} anisotropic all rest isotropic	2	1.0000	586	12.30
4						
	"	all anisotropic except C_7,C_8, C_{10},C_{11} and H atoms	2	.9874	406	9.97

5/

TABLE 10 (contd.)

Round	Hydrogens	Temperature Factors	Weights	k Scale factor applied to Fo	$\sum\omega\Delta^2 x10^{-5}$	R%
5	"	"	2	.9900	317	8.64
6	"	"	2	.9894	312	8.54
7	"	"	2	.9894	313	8.55

↓

~~3-D F_o-F_c map with hydrogens ommitted R = 10.8%~~

Note: Weighting schemes - No. 1 see Page 80

No. 2 see Page 81

TABLE 11

Bis (dimethyldithio carbamato-) pyridine zinc . $\frac{1}{2}$ benzene

Final co-ordinates and their estimated standard deviations.

	x/a	10^5 e.s.d.	y/b	10^5 e.s.d.	z/c	10^5 e.s.d.
Zn	.68246	8	.16932	19	.16484	6
S1	.78265	13	.15230	28	.29504	7
S2	.79566	13	-.06573	28	.17879	8
S3	.72354	14	.43973	29	.13614	8
S4	.61517	14	.19430	29	.03094	7
N1	.52658	33	.13040	76	.17741	21
N2	.91508	43	-.11196	92	.30686	28
N3	.66318	42	.50863	89	.00179	26
C1	.45455	48	.03815	98	.13302	28
C2	.34905	52	.01393	111	.13783	34
C3	.31584	51	.09186	115	.18990	42
C4	.39283	63	.19047	124	.23759	43
C5	.49595	52	.20515	110	.22911	32
C6	.83968	42	-.01623	101	.26518	30
C7	.96671	67	-.25390	136	.28127	42
C8	.95613	70	-.07600	138	.38155	45
C9	.66685	44	.39155	-97	.05027	28
C10	.61066	59	.47341	120	-.07124	38
C11	.70794	70	.67771	133	.01830	45
C12	.07521	54	-.11890	117	.03157	36
C13	-.01187	56	-.08218	118	.05702	33
C14	-.08763	55	.03453	117	.02623	36
H1	.4799		-.0226		.0911	
H2	.2905		-.0634		.1009	
H3	.2331		.0750		.1960	
H4	.3648		.2513		.2781	
H5	.5543		.2834		.2661	
H12	.1328		-.2178		.0582	
H13	-.0232		-.1491		.1020	
H14	-.1554		.0580-		.0488	

TABLE 12

VIBRATIONS

(i) Anisotropic

Temp. Factor = $\exp -(h^2B_{11} + k^2B_{22} + l^2B_{33} + klB_{23} + lhB_{31} + hkB_{12})$

	B_{11}	B_{22}	B_{33}	B_{23}	B_{31}	B_{12}
Zn	.00618	.01161	.00259	.00060	.00268	-.00055
S1	.00770	.01998	.00235	.00161	.00173	-.00453
S2	.00793	.01551	.00275	-.00171	.00398	-.00011
S3	.01042	.01290	.00263	.00060	.00072	-.00575
S4	.01010	.01915	.00215	-.00165	.00273	-.00241
N1	.00556	.01478	.00220	.00022	.00210	-.00093
N2	.00807	.02112	.00361	-.00071	.00295	-.00709
N3	.00861	.02238	.00273	.00381	.00200	.00145
C1	.00778	.01326	.00247	.00078	.00142	-.00281
C2	.00754	.02120	.00381	.00503	.00090	-.00546
C3	.00753	.01835	.00621	.00601	.00502	.00078
C4	.01062	.02469	.00569	-.00245	.00820	.00297
C5	.00828	.02226	.00323	-.00381	.00427	-.00154
C6	.00572	.01786	.00312	-.00184	.00426	-.00090
C9	.00668	.01650	.00264	.00025	.00330	.00133
C12	.00865	.02371	.00351	.00077	.00162	-.00280
C13	.00943	.02699	.00308	.00225	.00303	-.00683
C14	.00916	.02636	.00372	-.00023	.00473	-.00375

(ii) Isotropic

Temp. Factor = $\exp -(B \sin^2\theta/\lambda^2)$

	B (Å^2)
C7	6.77
C8	7.34
C10	5.96
C11	7.38
H1	3.80
H2	5.20
H3	5.80
H4	6.70
H5	5.10
H12	5.40
H13	5.00
H14	5.70

TABLE 13

(i) Bond Lengths with e.s.d.'s (Å)

Zn - S1	2.598	.004	Zn - S4	2.612	.004
Zn - S2	2.330	.004	Zn - S3	2.325	.004
Zn - N1	2.079	.006			
N1 - C1	1.320	.013	N1 - C5	1.342	.012
C1 - C2	1.379	.013	C4 - C5	1.367	.015
C2 - C3	1.376	.015	C3 - C4	1.413	.019
S1 - C6	1.707	.010	S4 - C9	1.707	.011
S2 - C6	1.727	.010	S3 - C9	1.732	.010
C6 - N2	1.333	.014	C9 - N3	1.342	.013
N2 - C7	1.466	.017	N3 - C11	1.465	.018
N2 - C8	1.484	.017	N3 - C10	1.473	.015

(ii) Angles (degrees)

S1 - Zn - N1	95.9	S4 - Zn - N1	93.9
S2 - Zn - N1	116.1	S3 - Zn - N1	116.8
S1 - Zn - S2	-73.4	S4 - Zn - S3	-72.9
S1 - Zn - S3	102.6	S4 - Zn - S2	102.1
S1 - Zn - S4	170.2		
S2 - Zn - S3	127.1		
Zn - N1 - C1	121.0	Zn - N1 - C5	120.7
C1 - N1 - C5	118.3		
N1 - C1 - C2	124.3	N1 - C5 - C4	122.5
C1 - C2 - C3	117.3	C3 - C4 - C5	118.3
C2 - C3 - C4	119.3		
Zn - S1 - C6	79.9	Zn - S4 - C9	80.4
Zn - S2 - C6	87.9	Zn - S3 - C9	88.9
S1 - C6 - S2	118.3	S4 - C9 - S3	117.3
S1 - C6 - N2	120.5	S4 - C9 - N3	123.3
S2 - C6 - N2	121.2	S3 - C9 - N3	119.4
C6 - N2 - C7	122.1	C9 - N3 - C11	123.9
C6 - N2 - C8	124.0	C9 - N3 - C10	119.5
C7 - N2 - C8	114.0	C10- N3 - C11	116.5

TABLE 14

Planarities of Groups.

(i) Pyridine

Least squares plane through N1, C1, C2, C3, C4 and C5.

Eqn: $+1.815x - 6.405y + 10.45z - 1.975 = 0$

Deviations from plane (Å) :-

N1	-.002	Zn	-.099
C1	-.005	S1	+1.55
C2	+.009	S2	-1.78
C3	-.006		
C4	.000		
C5	+.004		

(ii) Benzene

Least suares plane through the 6 atoms of benzene.

Eqn: $+5.019x + 5.648y + 9.231z = 0$

Deviations from plane (Å) :-

C12	+.0026	C12'	-.0026
C13	-.0027	C13'	+.0027
C14	+.0026	C14'	-.0026

(iii) Dimethyldithiocarbamate Groups

S1,S2,C6,N2,C7,C8 ligand		S3,S4,C9,N3,C10,C11 ligand	
$+9.945x + 4.723y - 7.657z = 6.238$		$+11.99x - 2.450y - 6.815z = 6.688$	
Atom	Deviation (Å)	Atom	Deviation (Å)
S1	-.005	S4	+.007
S2	+.005	S3	-.011
C6	-.005	C9	+.012
N2	+.016	N3	+.011
C7	-.023	C11	+.022
C8	+.010	C10	-.035
Zn	-.086	Zn	-.037
S3	-1.99	S2	+1.80
S4	-.56	S1	+.32
N1	+1.74	N1	-1.90

TABLE 15

Intermolecular Contacts below 3.90Å

Atom 1	-	Atom 2	Distance	Relation of Atom 2 to Atom 1 at position given in Table 11.
S1	-	C2	3.75	1 - x, $\frac{1}{2}$ + y, $\frac{1}{2}$ - z
S1	-	C3	3.76	'' '' ''
S2	-	C4	3.80	'' '' ''
S3	-	C3	3.86	'' '' ''
S3	-	C4	3.82	'' '' ''
C4	-	C6	3.75	'' '' ''
C8	-	C12	3.86	'' '' ''
N2	-	C3	3.77	1 - x, y - $\frac{1}{2}$, $\frac{1}{2}$ - z
C1	-	C5	3.77	'' '' ''
C2	-	C5	3.78	'' '' ''
C8	-	C14	3.77	'' '' ''
S2	-	C13	3.89	1 + x, y, z
S2	-	C14	3.83	'' '' ''
S2	-	C11	3.74	x, y - 1, z
S4	-	C1	3.68	1 - x, -y, -z
C9	-	C10	3.81	1 - x, 1 - y, -z
C11	-	C14	3.82	1 + x, 1 + y, z

See note opposite Page 8

Fig 16

Final 3D ($F_o - F_c$ map)

Contours at intervals of $\frac{1}{8}$th e's Å^{-3}

Zero and negative contours: - - - - - -

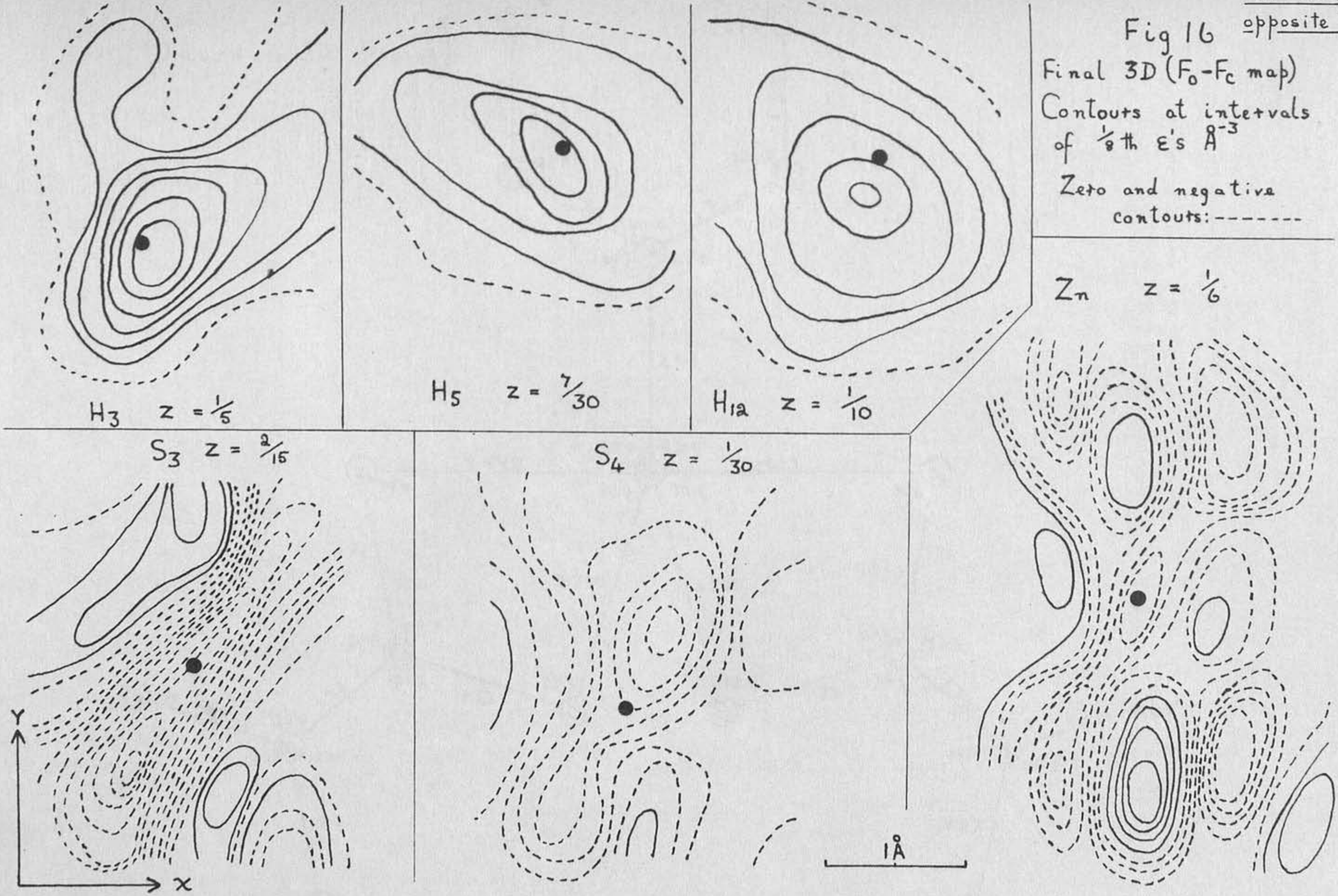


Fig 17

(Diagrammatic drawing)

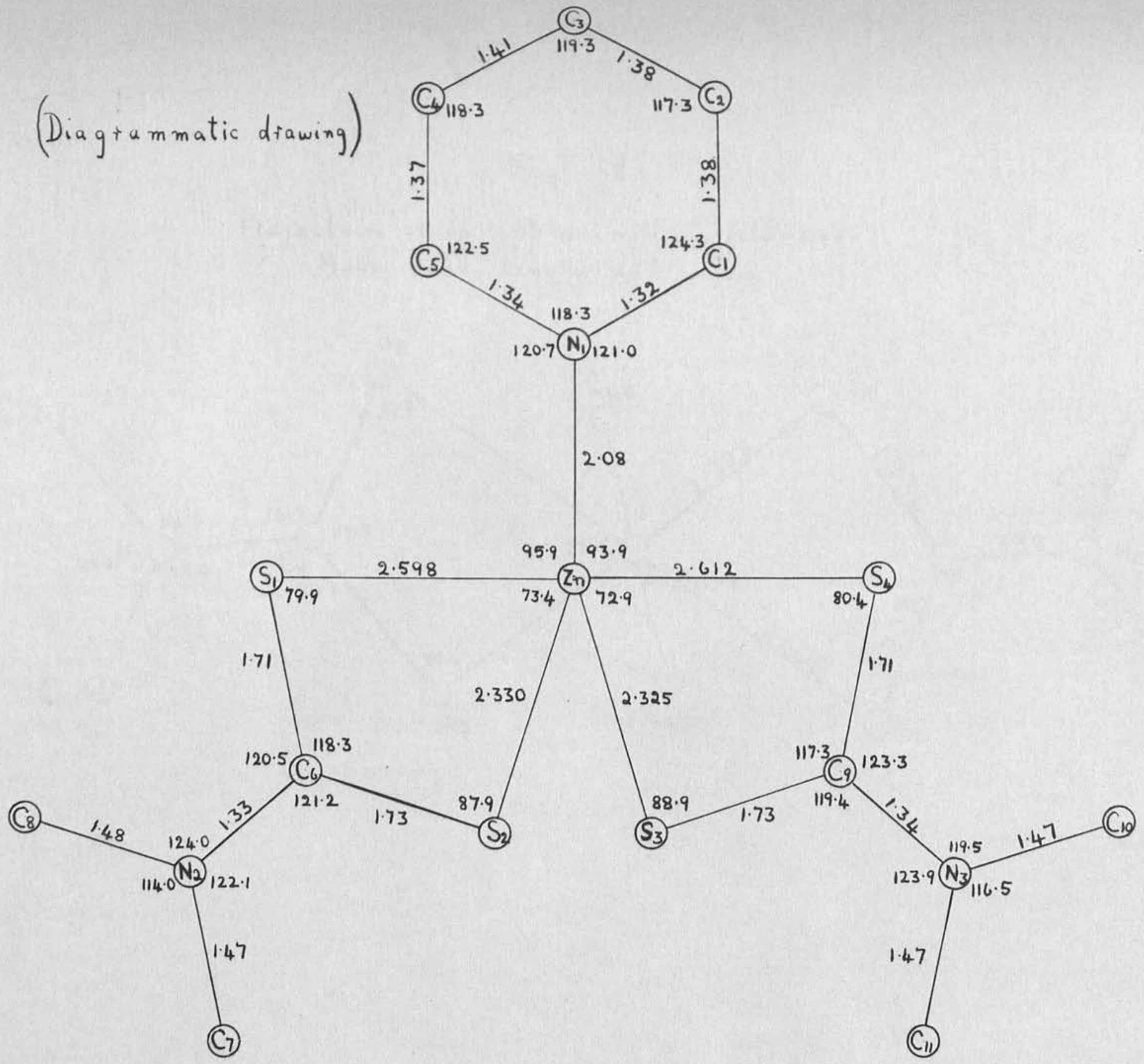


Fig 18

Projection along approximate 2 fold-axis
Mean bond lengths and angles.

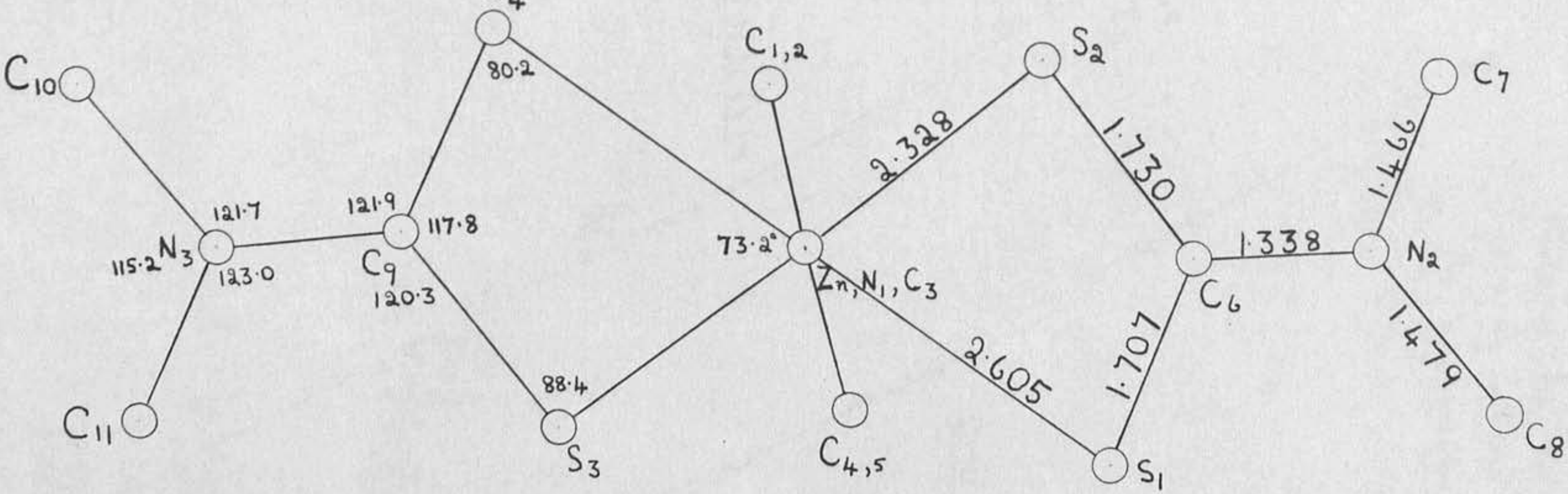


Fig 19

Plots of the mid-points of lines joining atoms related by the approximate 2-fold-axis

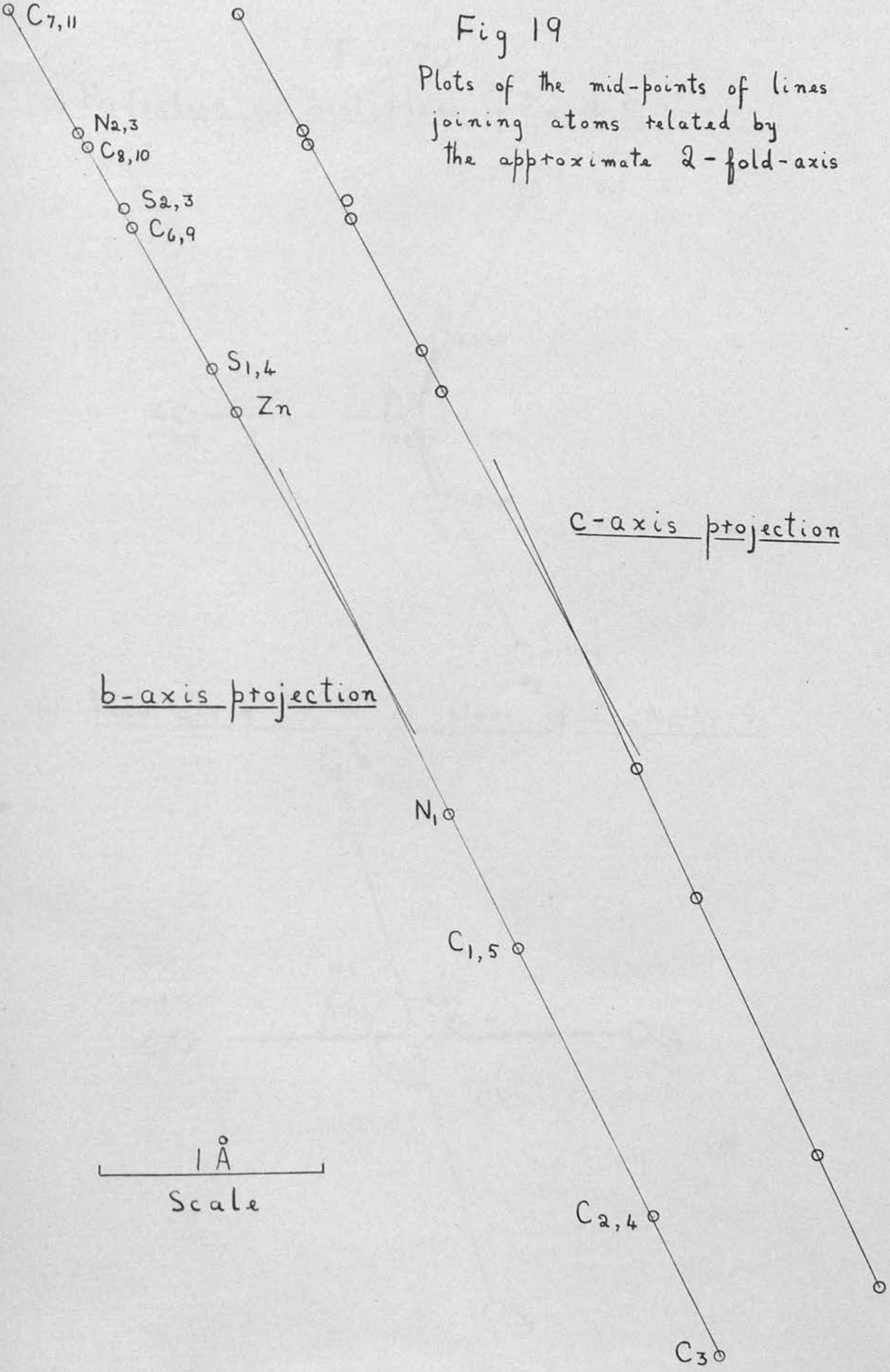
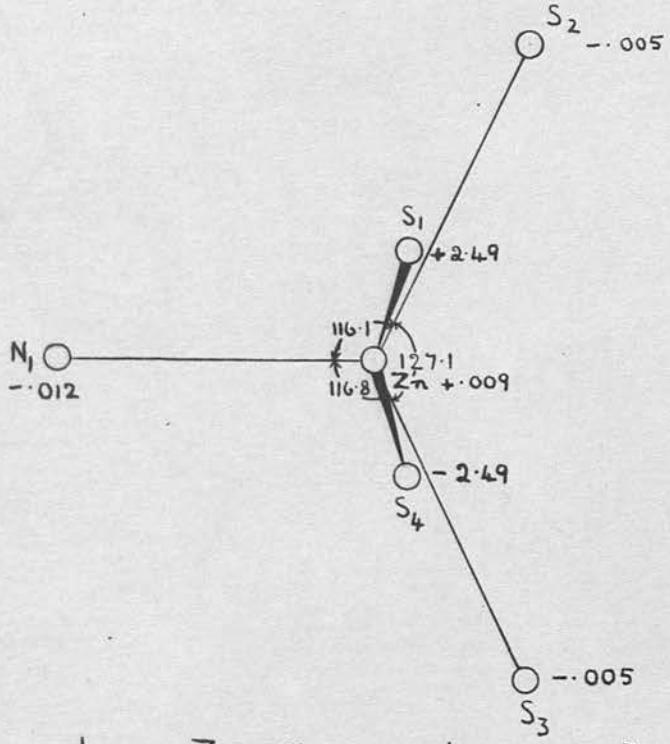


Fig 20

(i) Projection on best plane of Zn, N_1, S_2, S_3



(ii) View along Zn−N_1 in plane of Zn, N_1, S_2, S_3

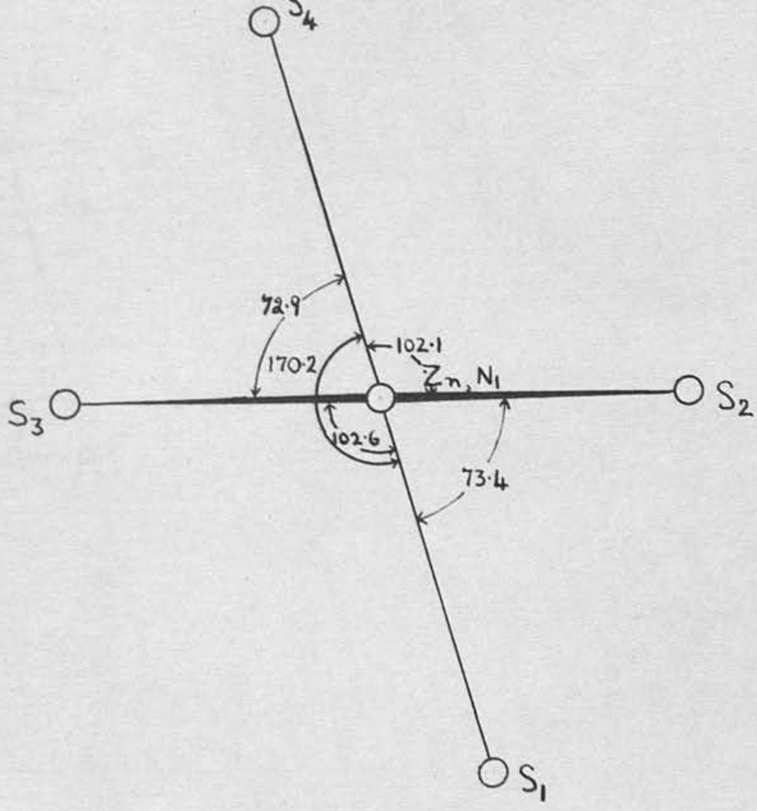


Fig 21 b-axis projection

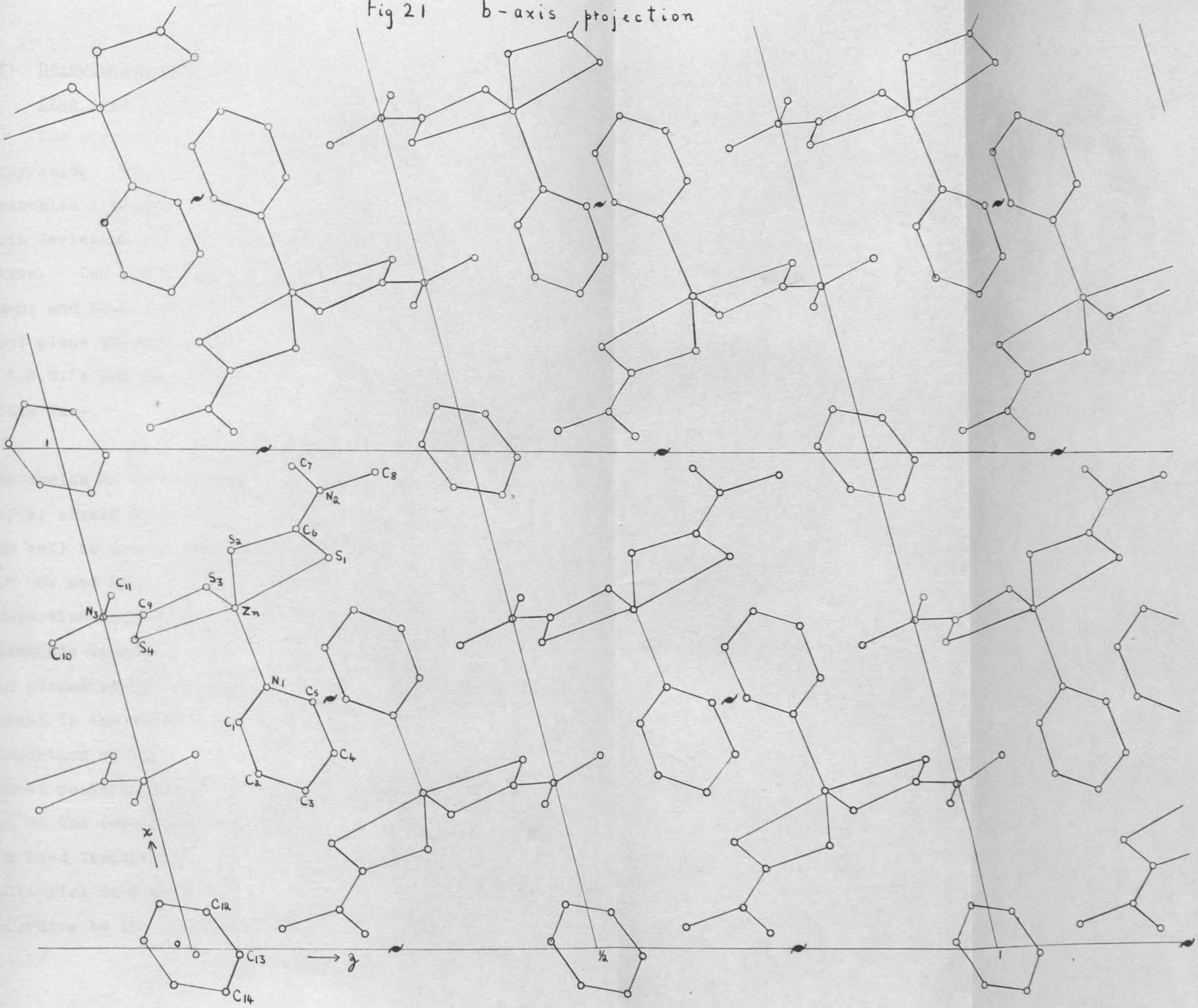


Fig 21

(f) Description and Discussion

Zinc coordination

The coordination of zinc is a rather distorted trigonal bipyramid. Examination of Figs. 18 and 20 shows that the structure resembles a trigonal bipyramid quite closely in some respects. The main deviation is the angle the axial bonds make with the equatorial plane. The equatorial plane passes through Zn, N_1, S_2 and S_3, and Zn-S_1 and Zn-S_4 are the two axial bonds. The deviations from the best plane through Zn, N_1, S_2 and S_3 (see Fig. 20) are all less than 2 E.S.D.'s and therefore not significant. The equation of this plane is:-

$$+ 1.184x + 1.720y + 18.38z = 4.121$$

The angles $N_1 \hat{Zn} S_2$ (116°), $N_1 \hat{Zn} S_3$ (116°) and $S_2 \hat{Zn} S_3$ (128°) differ significantly from the theoretical values of 120°, but this may well be due to interaction between the two bulky sulphur atoms.

S_1 and S_4 deviate by 17° from the true axial positions. This distortion is, of course, unavoidable due to the nature of the bidentate ligands and the Zn-S distances. It is noteworthy that the planes of the dimethyldithiocarbamate groups are approximately normal to the equatorial plane (see Fig. 20), thus reducing the distortion as much as possible. The small deviations from the normal position are in the direction expected if the deviations are due to the repulsions $S_1 \leftrightarrow S_3$ and $S_2 \leftrightarrow S_4$ ($S_1 \hat{Zn} S_3 = S_2 \hat{Zn} S_4 = 102°$). The bond lengths fit the trigonal bipyramidal model quite well. The equatorial Zn-S bonds are 2.33 Å while the axial Zn-S bonds are 2.60 Å. According to the theory of 5-coordination (see Introduction) longer axial/

axial bonds are to be expected due to electron pair repulsions. However in this case electron shifts may play an important part in causing the axial Zn-S bonds to be so long. (See following discussion).

The only other example of a truly trigonal bipyramidal zinc complex is terpyridyl zinc dichloride [59].

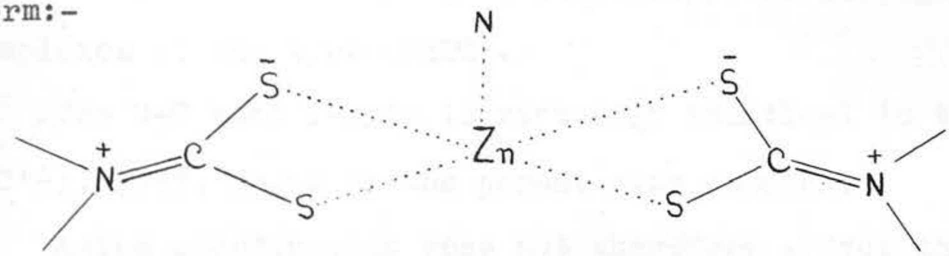
Zinc-Sulphur Bonds

The short Zn-S bonds of 2.33 Å ($Zn-S_2$, $Zn-S_3$) are about normal length (cf. Zn-S distances given in Introduction). The two long Zn-S bonds of 2.60 Å ($Zn-S_1$, $Zn-S_4$) are very much longer, and this could be due to electron pair repulsions and/or increase in the ionic character of the Zn-S bond.

In bis(diethyldithiocarbamato) Zn(II) [63], one of the ligands has Zn-S distances of 2.35 Å and 2.44 Å, while the other ligand has distances of 2.33 Å and 2.82 Å. This shows that a configuration with two dithiocarbamate groups coordinated to Zn, and with all Zn-S distances around 2.33 Å is unfavourable. This is probably due to electron pair repulsions. In (PZDC) the axial sulphur atom S_1, for example, might be repelled by bonding electron pairs associated with S_2, S_3 or N_1. Of these three, the repulsion of the $Zn-S_2$ electron pair must be the greatest ($S_1 \hat{Zn} S_2 = 73°$, $S_1 \hat{Zn} S_3 = 102°$). The repulsion of the $Zn-S_3$ bond pair is probably small, since it is known that the two sulphur atoms can approach zinc to 2.35 Å with $S \hat{Zn} S$ angles of 109° in Zn S [64] and 111° in Zn(II) dichlorobisthiourea [66].

While/

While electron pair repulsions probably play an important part, the substantial lengthening of the axial Zn-S bonds suggests that electron shifts of some sort take place, resulting in an increase in the ionic character of the axial bonds. Higgins and Saville [55] have carried out infra-red studies which have suggested such a change in Zn-S bonds, and they also obtained experimental evidence that there is an increase in the sulphur nucleophylic properties when an amine coordinates (see Introduction). All this evidence suggests strongly that there is a dominant contribution to the structure of complexes of the type (PZDC) by the form:-



This conclusion differs from that reached by Higgins and Saville (see Introduction) who proposed that all four Zn-S bonds are equally affected, and the N-C bond loses part of its double bond character on amine coordination.

The $Zn-N_1$ bond

The $Zn-N_1$ bond length is 2.079 Å (E.S.D. = ·006 Å). This is very similar to the value of 2.06 Å found in Zn(II) di-8-hydroxyquinolate dihydrate [57], but different from the values of 2.19, 2.11 and 2.37 Å found in zinc terpyridyl dichloride [59]. It is also slightly greater than the average Zn-N distance of 2.00 Å (max./

(max. limits 1.97 - 2.04) found in complexes with an imidazole nitrogen.

The N-C bond

The mean N-C bond length in (PZDC) is 1.338 (E.S.D. = .010 Å). This should be compared with the table of N-C bond lengths given in the Introduction. Comparison shows that the N-C bond length does not change when the alkyl group is varied from methyl to propyl. This agrees with the independent evidence of Chatt et al [69] based on I.R. studies (see Introduction). It is further evidence against the theory of Kerk et al [68] concerning the biological activity of complexes of the type (PZDC).

The N-C bond length is virtually identical to that of 1.33 Å (.019), [63], found in the parent zinc complex.

Amine coordination does not therefore affect the N-C bond in the way expected by Higgins and Saville (see Introduction). Their evidence depended on shifts in the I.R. absorption bands to lower frequencies when an amine coordinates. However as well as a shift in the band assigned to the N-C stretching vibration, there were several unexplained shifts in other bands on amine coordination. It seems possible that the shift in the N-C stretching band was produced by some cause other than reduction in N-C bond order, as proposed by Higgins and Saville. Their electron shift scheme which is given on page 51, must therefore be revised. The observed N-C bond lengths support the conclusion that the dominant contribution to the structure of (PZDC) is by the form given on page 86.

Dimethyldithiocarbamate ligands

The two ligands are planar within experimental error (see Table 14). The mean deviation from the best plane through S_1, S_2, C_6, N_2, C_7, C_8 is about 1 E.S.D., the maximum deviation (C_7) being less than 2 E.S.D.'s. Zn, however, lies at .086 Å from this plane which is certainly significant being about 16 (E.S.D.'s). The mean deviation from the S_3, S_4, C_9, N_3, C_{10}, C_{11} plane is about 1.5 E.S.D., with a maximum deviation (C_5) of just over 2 E.S.D.'s. Zn lies at .037 Å from this plane which is significant being about 7 E.S.D.'s.

This agrees with all other determinations which have all found the dithiocarbamate groups to be planar. A deviation of about .2 Å of the zinc atom from the planes of the ligands, has been found in bis(diethyldithiocarbamato) Zn(II) [63]. The deviations in (PZDC) are smaller but nevertheless constitute a significant departure from exact 2-fold symmetry in the complex. The distances from Zn to the planes of the two ligands are significantly different, and also the deviations are in opposite directions relative to the approximate 2-fold axis through Zn.

The mean S-C bond length in (PZDC) is 1.718 Å which agrees with the mean value of 1.72 Å found in bis(diethyldithiocarbamato) Zn(II) [63]. There seems to be a small, though barely significant, difference in the two types of S-C bond. S_1-C_6 and S_4-C_9 average 1.707 Å while S_2-C_6 and S_3-C_9 average 1.730 Å. This indicates that S_1 and S_4 are slightly more strongly bound to C_6 and C_9 respectively, than/

than S_2 or S_3, which agrees with the fact that S_1 and S_4 are more loosely bound to Zn.

The angles around C_6 and C_9 do not differ very significantly from the expected values of 120°, but those around N_2 and N_3 do. The angle made at N by the two methyl groups seems to be slightly less than the other two angles at N. This was also found in bis(diethyldithiocarbamato) Zn(II) where the Et $\hat{N}$ Et angle is 114°.

The observed N-CH_3 distances (1.466, 1.484, 1.473, 1.465) do not differ significantly from the average literature value of 1.479 Å for a C-N bond with a 4-covalent nitrogen [80].

Pyridine ring

The pyridine ring is accurately planar, all deviations from the best plane being less than $\frac{1}{2}$ E.S.D. (see Table 14). The deviation of Zn by nearly .1 Å from this plane is significant and is discussed later. The bond lengths (see Fig. 17) are all within 1.5 E.S.D.'s of the literature values [80], except N_1-C_1 (1.320 Å) and N_1-C_5 (1.342 Å). The average literature value for the latter two bonds is 1.37 Å. This is probably a significant difference, and may be connected with changes in the electron distribution due to the coordination of N_1 to Zn. The bond angles agree well with the literature values, and as expected the angles $N_1 \hat{C_1} C_2$ (124.3°) and $N_1 \hat{C_5} C_4$ (122.5°)-(lit. value 124°) - are greater than the $C \hat{C} C$ angles, (lit. value 118°).

Benzene ring

The benzene ring is very accurately planar the deviations being only/

only about $^1/_5$ E.S.D. and therefore quite insignificant. The bond lengths (1.365, 1.363 and 1.388 Å) are all within 2 E.S.D.'s of the literature value of 1.39 Å, and the angles do not differ significantly from 120°.

It should be noted that pyridine might well replace benzene on the centres of symmetry in the crystal. Both pyridine and benzene were present in the solution from which the crystals were obtained, although only a trace of pyridine was present. It would probably not be possible to detect the difference between pyridine and benzene by X-Ray methods, especially if the pyridine is orientated at random.

2-Fold symmetry of complex

There is an approximate 2-fold axis though Zn, N_1 and C_3 of pyridine. Fig. 19 gives a plot of the mid-points of lines joining atoms related by this axis. The zinc dimethyldithiocarbamate part of the molecule gives a fairly good straight line plot, with deviations all less than .01 Å, except for the mid-point of the S_2-S_3 line which deviates by about .03 Å from the best line.

The pyridine ring also gives a good straight line plot with deviations all less than .01 Å, and therefore not significant.

The equations of these lines are as follows:-

(i) Zn dimethyldithiocarbamate axis	$x - 3.637y = + .0667$ $x + 10.283z = + 2.378$
(ii) Pyridine ring axis	$x - 5.468y = - .1865$ $x + 16.995z = + 3.542.$

Both/

Both lines meet at the point (.580, .141, .174) which lies about .7 Å from N_1, and exactly mid-way between C_3 and the mid-point of C_7-C_{11}. The angle between these lines is 4.0° which is certainly a significant deviation. The direction in which the 2-fold axis is "bent" is approximately normal to the pyridine ring and towards S_3. This results in a slightly shorter contact with S_4 than with S_1 (C_1-S_4 = 3.48 Å; C_5-S_1 = 3.55 Å).

The cause of this distortion is the fact that the pyridine ring has close contacts with neighbouring molecules on one side and not on the other. Inter-molecular contacts are listed in Table 15. The pyridine rings of molecules related by the 2-fold screw axes are roughly normal to one another, and the "edge" of one ring contacts the "plane" of the next one. The important contacts are probably those from C_5 of the 2-fold screw axis-related molecule to C_1 (3.77 Å) and C_2 (3.78 Å). Several other contacts with neighbouring sulphur atoms are all on the same side of the ring, but the closest contact of 3.68 Å from C_1 to S_4 acts roughly in the plane of the ring, and so cannot be wholly responsible for the distortion.

Another significant departure from 2-fold symmetry is the difference in the position of the Zn atom relative to the two dithiocarbamate ligands. This has been discussed previously. It may be connected with the slight deviation of the S_2-S_3 mid-point from the axis (see Fig. 19), and the distortion of pyridine from the axial position.

There/

There seems to be no reason to suppose that the complex cannot be exactly symmetric in solution or in the other crystalline form (see Part II.2.). The difference in the orientation of pyridine (cf. Figs. 10 and 18) in the two crystals, and the distortion of pyridine from the true axial position, suggests that, although N_1 is strongly bound to Zn, there is a certain amount of flexibility in the position of the ring. It is very likely that weak forces, of the order of Van der Waals' forces, acting on the end of the ring would be sufficient to produce quite a large levering effect. It is noticeable that in neither of the two crystals does the pyridine take up a position so as to minimise its contacts with S_1 and S_4.

Accuracy of the Determination

The final value of R (excluding reflections too weak to be observed) was 8.54%. R for those unobserved weak reflections listed in Appendix III(b) was 57%, and R for observed and unobserved reflections was 10.7%. These values could probably have been improved by taking into account the 12 methyl hydrogens omitted from the calculations. Also there is some evidence of extinction affecting the most intense reflections. If those reflections marked 'E' in Appendix III(a) are omitted, R (observed reflections only) becomes 8.10%.

The estimated standard deviations obtained from the least squares matrix (block diagonal approximation), should be fairly good estimates, since the structure is centrosymmetric, and there are no atoms/

atoms on special positions. The approximate molecular, but non-crystallographic, 2-fold axis through the complex, means that there have been two partly independent measurements of bond lengths related by the axis. The E.S.D. of the mean bond length may be calculated by the formula:-

$$6^2(\mathrm{M}) = \frac{6^2\,(\mathrm{A})\,.\,6^2\,(\mathrm{B})}{6^2\,(\mathrm{A}) + 6^2\,(\mathrm{B})}$$

where: $6^2(\mathrm{M})$ is variance of mean bond length. $6^2(\mathrm{A})$, $6^2(\mathrm{B})$ are variances of related bond lengths,

and since $6^2(\mathrm{A}) \div 6^2(\mathrm{B})$

$$6(\mathrm{M}) = \frac{6(\mathrm{A})}{\sqrt{2}}$$

Since the complex is slightly distorted, especially about the co-ordination centre at Zn, it is probably not justifiable to use this formula for those bonds involving Zn.

Packing

The packing of molecules is illustrated in projection along the b-axis in Fig. 21. The crystal is held together by Van der Waals' forces with contacts ranging from about 3.7 Å upwards. The minimum intermolecular contact is 3.68 Å (C_1-S_4). Table 15 lists all intermolecular contacts below 3.90 Å.

The main feature of the packing is the large cylindrical space parallel to b between benzene molecules. The distance between benzene molecules along y is about 8 Å, and only two contacts with C_8 of neighbouring molecules, seems to prevent the benzenes from moving/

moving up and down these spaces. This easy route of escape for benzene probably accounts for the instability of the crystals.

As far as the packing of the complexes is concerned, it is moticeable that there are no important contacts between (PZDC) molecules across the planes $^{x}/_{a} = 0, 1, 2 \ldots\ldots$ i.e. there are no important contacts over the cell boundaries along the x direction. The benzenes appear to act as buffers between molecules along this direction. The packing within a cell is not very compact, and there are no plane-plane contacts as might be expected. The pyridines are in contact but their planes are normal to one another.

Vibrations

Table 12 gives the anisotropic vibrations of each atom. There is no noticeable anisotropy among the heavy atoms. Zn has an average B = 3.5 $\mathring{A}^2$ while the S atoms average B = 4.5 $\mathring{A}^2$. There is a tendency for vibrations to increase towards the "ends" of the molecule. Thus C_6, C_9 average 4.0 $\mathring{A}^2$, N_2, N_3 5.1 $\mathring{A}^2$, and the methyl carbons 6.9 $\mathring{A}^2$. There is a similar increase in vibration towards C_3 of pyridine, but here there is some anisotropy. C_3 has the highest 'B' of 9.8 $\mathring{A}^2$ along z, and this fits in with the fact that it has no contacts along this direction. The benzene ring vibrations, surprisingly, are less than those of the methyl carbons. They average 5.5 $\mathring{A}^2$ along x, 6.6 $\mathring{A}^2$ along y and 5.2 $\mathring{A}^2$ along z, the greater vibration along y agreeing with the loose packing along this direction. Generally the fairly high 'B' values reflect the weakness of the forces holding the molecules together.

(g) Conclusions

The complex (PZDC) is a 5-coordinate zinc complex with a distorted trigonal bipyramidal configuration. The two axial Zn-S bonds average 2.60 Å, with the two equatorial Zn-S bonds, 2.33 Å and Zn-N_1 2.08 Å. The equatorial bonds are of normal length, but the two axial bonds are considerably longer than usual. This is probably due to a combination of electron pair repulsions, and a weakening of the axial Zn-S bonds due to the coordination of pyridine. The mean N-C bond length in the dithiocarbamate groups is 1.338 Å, which is very similar to the lengths found in all other dithiocarbamate complexes, and indicates about 84% double bond character. This agrees with the experiments of Chatt et al [69] and is further evidence against the theories of Kerk et al [68]. Both the Zn-S and the N-C bond lengths show that the electron shift scheme for amine coordination proposed by Higgins and Saville, must be revised. The coordination of an amine appears to affect only two of the four Zn-S bonds, and has no effect on the N-C bond.

In agreement with other determinations, the dimethyldithiocarbamate groups are both planar and the bond lengths and angles are all normal. Zn, however, lies slightly out of the plane of both ligands, and its position is different relative to each. The Me $\hat{N}$ Me angle is slightly less than 120° as has been found also by Vaciago et al [63]. This is probably due to repulsion of the methyl groups by the sulphurs.

There is an approximate two-fold axis through Zn, N_1 and C_3, but/

but the axis of the pyridine ring deviates by 4° from the axis of the rest of the molecule. This is caused by Van der Waal's contacts in the crystal. The difference in the deviations of Zn from the dithiocarbamate planes may be connected with this. It is very probable that the complex can assume accurate two-fold symmetry in solution. The orientation of pyridine is obviously largely dependent on intermolecular forces, since it is different in the crystals without benzene of crystallisation.

The crystals with benzene of crystallisation, consist of two types of complex, D and L. The packing is rather irregular, and there are some large empty spaces especially between benzene molecules along the y-axis.

COMPUTING METHODS

In the course of this work, the following programs were used:-

(1) Structure factor, Fourier and data reduction programs written by J.S. Rollett for D.E.U.C.E. (Glasgow). Basic machine code.

(2) SFLS program written by J.S. Rollett for use on Mercury (Harwell). Basic machine code. Very similar to SFLS Diamand/ Harding (see below).

(3) A series of programs written by M.M. Harding for use on Atlas (Manchester and N.I.R.N.S., Harwell):-

(i) 8/2 Lp correction and modification of data (EMA)

(ii) 3/5 Centrosymmetric fourier projections (EMA)

(iii) Molecular Geometry - calculations of best planes by least squares and projections of structures (AA)

(iv) 7/7 Combined structure factors and fourier program, allowing data to be read from magnetic tape. A later version (7/8) was able to accept anisotropic temperature factors. (EMA)

(4) SFLS Diamand/Harding - a program written by R. Diamand in EMA, and modified to accept data from magnetic tape, etc., by M.M. Harding. It had the following facilities:-

(i) Any space group possible.

(ii) f curves tabulated at 32 values of Sin^2 θ.

(iii) Isotropic, anisotropic or a mixture of both types of temperature factor acceptable.

(iv) Weighting scheme such that $\sqrt{w} = 1$ if $F_o \leqslant F^*$, and otherwise/

otherwise $\sqrt{w} = F^{*}/F_o$. F^{*} given in input data.

(v) The omission of certain atoms (e.g. hydrogens) from the least squares operation was possible.

(vi) Block diagonal approximation.

(vii) Any number of cycles possible.

(viii) Allowance made for the interaction between scale factor and the overall temperature factor.

(ix) Coordinate variances, $6^2(p)$, output, calculated from the appropriate diagonal element of the matrix, a_{ii} using:-

$$6^2(p) = \frac{1}{a_{ii}} \cdot \frac{\sum w\Delta^2}{m-n}$$

Where m = no. of observations

n = no. of parameters.

(5) A bond lengths and angles program written by O.S. Mills for use on Atlas (AA).

(6) The following two programs were written specially for this work by the author, for use on Atlas:-

(a) Fraser 2/5 (AA)

A structure factor program, written for space group $P2_1/c$, but easily modifiable to take all centrosymmetric space groups of higher symmetry. It had the following facilities:-

(i) f curves could be tabulated at any convenient equal intervals of Sin θ , the degree of subdivision being indicated for each f curve as read in.

(ii) Data acceptable in the form F_o or $F_o{}^2$. If $F_o{}^2$ then a modification function could be applied which was tabulated/

tabulated as a function of Sin .

(iii) Scaling of F_o either by a given scale factor or using the factor $\sum Fc/\sum Fo$. Separate scaling of different batches of data (e.g. k = 0, 1 ..... etc.) was also possible.

(iv) All reflections with Sin $\theta \geqslant 1$ printed out.

(v) All reflections with poor agreement between F_o and F_c printed out.

(vi) Any number of consecutive jobs possible.

(vii) The output could be transferred directly to magnetic tape for storage purposes.

(b) Fraser 3/2 (AA)

A program to calculate the E.S.D.'s of bond lengths from the coordinate variances obtained from SFLS Diamand/Harding. The formula used ignored covariances of coordinates, but took into account the E.S.D.'s of cell dimensions. In the general case, (triclinic system), a bond length is a function of 12 variables, all of which have an E.S.D. In general:

if Z = f(A,B,.....) i.e. if Z is a function of A,B .....

$$\text{Then} \quad 6(Z) = \sqrt{\left[6(A)\frac{\partial A}{\partial Z}\right]^2 + \left[6(B)\frac{\partial B}{\partial Z}\right]^2 + \cdots}$$

The expression for a bond length (S) was treated in this way, and a value of 6(S) derived. A simple modification and extension would have allowed the calculation of bond angle E.S.D.'s.

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My thanks are also due to the appropriate authorities for the free use of Mercury and Atlas at N.I.R.N.S., Harwell and Atlas at Manchester. The use of programs written by J.S. Rollett, O.S. Mills and R. Diamand is gratefully acknowledged. Thanks are also due to Professors Sir Edmund Hirst, F.R.S., and T.L. Cottrell for laboratory facilities.

I should also like to thank my wife and Miss Hazel Hamilton for typing this thesis.

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List of A_o, B_o, A_c, B_c for Ni (histidine)$_2$. H_2O

APPENDIX I

(unobserved reflections marked *)

h ℓ	k A_o	B_o	A_c	B_c
0	0			
2	2210	396	2063	369
4	815	-338	732	-303
6	650	146	640	144
8	105	-52	65	-33
0	2			
0	1338	0	1417	0
2	2049	-380	2325	-431
4	1481	215	1286	187
6	664	-169	617	-157
8	263	-16	269	-16
0	4			
0	319	0	443	0
2	1372	-136	1260	-125
4	1270	-569	1264	-566
6	500	-155	427	-133
8	304	-102	333	-112
0	6			
0	980	0	978	0
2	1401	-353	1303	-329
4	451	-122	378	-102
6	219	-237	235	-253
8	315	17	307	17
0	8			
0	847	0	1230	0
2	311	170	229	125
4	487	36	478	35
6	488	225	437	202
8	13	-58	11	-50
0	10			
0	381	0	442	0
2	380	53	495	70
4	240	246	208	213
6	156	-95	130	-79
0	12			
0	91	-0	121	-0
2	184	81	103	45
4	147	-152	153	-159
0	14			
2	104	-201	46	-89
4	140	58	122	51
1	1			
1	1576	77	1814	88
3	177	62	190	67
5	613	20	609	20
7	309	62	271	54
9	78	16	84	17
1	2			
2	-609	-945	-587	-911
4	-341	-571	-303	-507
6	30	-97	29	-92
8	64	7	62	7
1	3			
1	-47	-112	-23	-54
3	1227	81	1204	80
5	546	143	496	129
7	277	19	275	18
9	158	-6	168	-6
1	4			
0	-793	-0	-724	-0
2	-386	-98	-359	-91
4	-52	-118	-47	-106
6	5	-111	4	-93
8	-58	-55	-48	-45
1	5			
1	652	91	636	89
3	907	4	871	3
5	88	-34	93	-36
7	177	-17	200	-19
9	219	48	201	44
1	6			
0	164	-0	142	-0
2	246	347	185	261
4	-66	82	-58	71
6	-251	-65	-233	-60
8	-151	-56	-126	-47
1	7			
1	714	-26	575	-21
3	145	33	205	47
5	377	39	333	35
7	210	73	208	72
9	35	8	52	13
1	8			
0	123	-0	140	-0
2	74	-64	56	-49
4	-169	-19	-143	-16
6	-131	14	-116	13
8	-64	16	-64	15
1	9			
1	254	15	298	17
3	87	74	104	89
5	399	136	375	128
7	158	9	112	6
1	10			
0	-173	-0	-207	-0
2	-149	-109	-213	-156
4	-21	-132	-13	-84
1	11			
1	285	39	291	40
3	181	46	156	40
5	17	-78	11	-51
1	12			
0	-143	-0	-62	-0
2	-105	-37	-67	-23
4	-78	-82	-86	-90
1	13			
1	-59	-1	-81	-1
3	291	-73	199	-50
5	56	27	86	41
1	14			
2	-47	48	-29	29
4	21	30	15	22

```
 1   15
3      55      60      50      54
 2   0
0     862      -0     719      -0
2    -616     133    -411      89
4     365    -341     331    -310
6     735    -177     660    -159
8     110      25      84      19
 2   1
1     801     269     798     267
3    -865    -635    -703    -516
5      61    -125      52    -107
7     -54      51     -64      62
9      32     -16      21     -11
 2   2
0     234       0     262       0
2     349     -61     412     -72
4     515      34     522      34
6     385      34     351      31
8     194       1     171       1
 2   3
1    -441    -796    -375    -678
3  *  -19       3     -23       4
5    -141     -62    -113     -50
7      93     -37      82     -33
9     -35      26     -40      29
 2   4
0     480       0     598       0
2    1247     113    1206     109
4     461     261     484     274
6      -9     164      -9     168
8     224      -1     235      -1
 2   5
1    -304     547    -255     459
3    -133     -80    -117     -70
5     122      11     138      13
7    -162     -15    -136     -13
9     -32     -65     -29     -59
 2   6
0     644       0     729       0
2     751     154     796     163
4     381      66     393      68
6     134      -3     157      -3
8     128      31     139      34
 2   7
1     109    -212      99    -191
3     171     119     155     107
5    -416    -114    -387    -106
7     -63     -86     -58     -79
9      -9      23     -15      39
 2   8
0     307       0     508       0
2     111     -67     173    -104
4     405    -131     389    -125
6     497     -61     411     -51
8      36      12      37      13
```

```
 2   9
1     -60      33    -132      73
3    -259    -218    -227    -191
5     116      16     125      18
 2   10
0     380       0     497       0
2     163     -70     277    -119
4     230     -94     197     -80
6     216     -77     178     -63
 2   11
1    -103    -136    -112    -148
3       5      20       9      37
5     -51     -55     -42     -45
 2   12
0     298       0     337       0
2     441     -12     378     -10
4     160     -41     167     -42
 2   13
1     120     109     118     108
3     -63     -47     -82     -61
5      -5     -37      -8     -58
 2   14
2     405      28     254      18
4     282      12     215      10
 2   15
3     152      76     121      61
 3   1
1     197     233     222     262
3      54     249      32     146
5     625     -23     638     -23
7     282      23     257      21
9      54      26      60      29
 3   2
0    1343      -0    1180      -0
2      73     496      67     451
4    -208     207    -171     171
6       0      49       0      15
8     -62      15    -115      27
 3   3
1     457    -128     560    -157
3     633       9     655       9
5     109     205      99     186
7     206      68     189      62
9     182     -10     185     -10
 3   4
0    -513       0    -523       0
2    -269      50    -198      37
4     124     164     141     185
6     109     139     101     129
8     -33      11     -29      10
 3   5
1     407       5     426       6
3     761     173     731     166
5     103     121      98     114
7     168      22     189      25
9     155     -18     157     -18
```

```
  3     6
 0    -439      -0     -329     -0
 2    -121    -145      -76    -90
 4    -114     -87     -114    -87
 6    -130     -25     -124    -24
 8      97      -4      103     -5
  3     7
 1     489     131      433    116
 3     272       7      308      8
 5     449     -84      401    -75
 7     157     -29      168    -31
  3     8
 0    -199      -0     -212     -0
 2    -121     -15     -102    -13
 4    -101     -61     -120    -73
 8      19      13       36     24
  3     9
 1     295     -58      472    -92
 3     193    -106      178    -98
 5     374     -78      345    -72
 7     206      -0      158     -0
  3    10
 0    -101      -0     -173     -0
 2    -104      36     -150     52
 4      83     105       98    124
 6      91      74       74     60
  3    11
 1     380     -19      396    -20
 3     232     -26      303    -34
 5     174      47      155     41
  3    12
 0     288      -0      285     -0
 2      84      62       74     54
 4     -90      11     -122     14
  3    13
 1     382      26      292     20
 3     449      25      324     18
 5      68     -25       75    -28
  3    14
 2       0     -85        0    -73
 4      49     -43       48    -42
  3    15
 3     246     -42      163    -28
  4     0
 0    1247       0     1211      0
 2    1216    -153      992   -125
 4     591     214      597    216
 6     555    -116      526   -110
 8      85      14       80     13
  4     1
 1     445     410      459    423
 3    -337     229     -325    221
 5      34     -63       45    -84
 7     -53     -34      -57    -37
 9     -38      13      -56     19
```

```
  4     2
 0    2005       0     1954      0
 2     639     107      638    106
 4     604    -368      592   -361
 6     323      30      334     31
 8     101     -62      109    -67
  4     3
 1    -160     195     -137    166
 3    -194     236     -186    227
 5     155      70      151     69
 9     -53       4      -61      5
  4     4
 0    -415       0     -198      0
 2    1381    -490     1246   -442
 4     500      31      526     32
 6     155    -241      140   -218
 8     270     -28      307    -32
  4     5
 1    -404    -167     -347   -144
 3     -26     -57      -35    -76
 5     -42     114      -45    124
 7      55      82       50     74
 9      45     -21       59    -27
  4     6
 0     701       0      685      0
 2     380      98      399    103
 4     647    -240      589   -218
 6     322      15      328     15
 8     147     -80      146    -80
  4     7
 1    -154      18      -97     11
 3      23      17       21     15
 5    -210     -26     -221    -27
 7      37      14       28     11
  4     8
 0     571       0      861      0
 2     663     -97      650    -95
 4     227      62      232     63
 6     267    -128      248   -119
 8      82      27       93     30
  4     9
 1    -148      63     -203     86
 3     -41     111      -37    101
 5     132      78      122     72
 7      -6      25      -10     45
  4    10
 0     603       0      665      0
 2     192      37      265     50
 4     402     -54      361    -49
 6     260     102      257    101
  4    11
 1      63      28       42     19
 3     -82     104      -87    110
 5      -1      72       -1     70
```

```
 4    12
0       68      0      47      0
2      499    -13     399    -11
4      213     81     257     97
 4    13
1       66    -12      80    -15
3      -98    -61     -89    -56
5      -73    -22     -96    -29
 4    14
2      283     59     181     37
4      180   -169     119   -112
 4    15
3       72    -64      67    -60
 5     1
1      596   -108     657   -119
3       49    -52      88    -93
5      369     13     377     13
7      168     43     172     44
9       33    -27      40    -33
 5     2
0      803     -0     707     -0
2     -256    165    -259    168
4     -110   -102     -97    -91
6      171   -104     176   -107
8      -38      0     -76      1
 5     3
1      437     78     504     90
3      598    -38     577    -37
5       92   -102     109   -121
7       74    -61      98    -81
9      123     49     118     47
 5     4
2      -23   -181     -23   -177
4      156    -30     139    -27
6       86     50      85     49
 5     5
1     -121    -46     -45    -17
3      622     56     663     60
5      303     51     306     52
7      173      6     188      6
9       67      0      97      0
 5     6
0      -46     -0     -18     -0
2      423     14     388     13
4       81     57      70     49
6      -74     15     -85     17
8      104     -1      97     -1
 5     7
1      595     17     562     16
3      113     30     191     51
5      198     82     204     85
7      158     49     150     46
 5     8
0       74     -0     119     -0
2      188    104     176     97
```

```
4       99     10     109     11
8       21     13      34     22
 5     9
1      338     14     502     20
3       75     58      78     61
5      174     22     171     21
7      134     56     122     51
 5    10
0      136     -0     105     -0
2        0    -20       0    -41
4       49     20      69     28
6      139     22     115     18
 5    11
1      -53     27     -82     41
3      223     66     264     79
5      274    110     278    112
 5    12
0      161      0     191      0
2      -21     33     -11     17
4      -18      7     -38     14
 5    13
1      217     65     164     49
3      241     92     144     55
5       18    -20      19    -21
 5    14
2       43    -35      23    -19
4       18    -26      13    -20
 5    15
3      111    -22      61    -12
 6     0
0     1061      0    1026      0
2      557   -175     598   -188
4      670    -16     625    -15
6      522     53     523     53
8      124    -17     158    -21
 6     1
1      343   -362     336   -354
3      -65    223     -57    198
5      -45    -27     -12     -7
7      124    -14     115    -13
9      -36     17     -40     19
 6     2
0     1532     -0    1430     -0
2      938      6     893      6
4      458   -146     483   -154
6      303    -66     306    -66
8      165    -12     154    -11
 6     3
1      871    263     801    242
3     -303   -254    -289   -242
5      337    -12     351    -12
7      -14     65     -16     71
9      -17    -23     -21    -30
 6     4
0      335     -0     429     -0
2     1058    -13     989    -12
```

```
4     621     32    643     33
6     185    -76    183    -75
8     173      0    194      0
 6    5
1     225   -305    214   -291
3     749     68    693     63
5     -55    -75    -28    -39
7      58    -67     64    -74
9      18     25     25     34
 6    6
0     526      0    500      0
2     506    -21    552    -23
4     560     43    506     39
6     301     81    308     83
8     129     -4    140     -4
 6    7
1     248    248    257    257
3     346    -88    329    -84
5     153    -58    155    -59
7      23    -19     28    -24
 6    8
0     580      0    895      0
2     468     -2    451     -1
4     122    -28    132    -30
6     181    -55    168    -51
8      84      6    100      7
 6    9
1     199   -166    283   -236
3     201    -61    197    -60
5      21    -50     31    -74
7      93    -18    111    -22
 6   10
0     215      0    218      0
2     164     -6    181     -6
4     297    -26    272    -23
6     215     18    202     17
 6   11
1     314     67    264     56
3     -43    -65    -53    -81
5     220      3    204      3
 6   12
0     -34     -0     -5     -0
2     297     13    192      9
4     181     31    209     36
 6   13
1      41    -22     33    -18
3     210    165    159    125
5      17     17     22     22
 6   14
2     272     30    160     18
4     -12    -68    -10    -54
 6   15
3      82    -92     45    -51
 7    1
1     880    203    933    216
3     675    235    696    242
```

```
5     682    168    633    156
7     308     77    295     74
9      91      5    118      6
 7    2
0     768     -0    715     -0
2    -294    -51   -266    -46
4     -95     13    -79     11
6     271     90    254     84
8     -25      5    -60     13
 7    3
1     846    -21    919    -23
3     639     61    656     62
5     311     23    299     22
7     289     26    280     25
9     174     33    196     37
 7    4
0     582     -0    491     -0
2     218    -60    193    -53
4      34    -85     33    -83
6     -26    -47    -22    -41
 7    5
1     316   -121    315   -121
3     604    -94    592    -92
5     397     67    387     66
7     263     34    254     33
 7    6
0    -484     -0   -411     -0
2     308     60    291     56
4     258     21    219     18
6     -85    -59    -67    -46
 7    7
1     545     45    456     37
3     332     53    330     52
5     277    -40    263    -38
7     156    -23    162    -24
 7    8
0      19     -0     26     -0
2     132    -44    113    -38
4      47    -30     59    -38
8      32    -11     63    -22
 7    9
1     307     52    472     80
3     230     18    178     14
5     178    -38    153    -33
7      94    -29     65    -20
 7   10
0     412      0    384      0
2      17    -83     21   -107
4    -110   -113    -83    -85
6      71    -29     72    -29
 7   11
1     183   -131    126    -90
3     211    -43    234    -48
5     173     35    149     30
```

```
 7     12
0      -34      -0     -37      -0
2      -60      42     -39      27
4       82      50     111      67
 7     13
1      266      30     183      21
3      201     -78      90     -35
5        3     -56       3     -54
 7     14
2      104      89      77      66
4       47      20      15       6
 8      0
0     1102       0    1087       0
2      566     326     584     337
4      806    -139     812    -140
6      419      91     441      96
8       74     -10      75     -10
 8      1
1     -425     -60    -374     -53
3     -263     -11    -264     -11
5      236      18     230      18
7       86      -7      75      -6
9      -51     -14     -54     -15
 8      2
0      652       0     698       0
2     1005     -42     993     -41
4      455     219     451     217
6      321     -69     316     -68
8      244      30     235      29
 8      3
1      -82      50    -114      70
3     -517    -105    -551    -112
5       75     -69     118    -107
7       24      17       9       6
 8      4
0     1028       0    1023       0
2      489     -45     489     -45
4      433    -127     447    -131
6      295     129     280     123
8      189     -23     194     -24
 8      5
1     -193     -43    -224     -50
3       63      87      35      49
5     -239      29    -270      33
7      -86     -12     -80     -12
 8      6
0      258       0     183       0
2      626    -194     628    -195
4      400      67     387      65
6      209     -84     218     -88
8      123      22     137      25
 8      7
1     -378      85    -363      82
3       76     155      74     151
5      -89     138    -108     168
7      -46      65     -47      66
```

```
 8      8
0      386      -0     606      -0
2      261     255     234     229
4      281    -110     276    -108
6      218     -31     176     -25
 8      9
1        3      20       4      23
3     -232      79    -180      61
5     -103      -4    -124      -5
 8     10
0      273       0     226       0
2      248    -106     338    -144
4      160      32     132      26
6      103     -38      80     -30
 8     11
1     -133     -29    -121     -26
3     -203     -57    -231     -65
 8     12
0      378       0     266       0
2      211     -78     114     -42
4      123     -80     130     -84
 8     13
1     -247     -35    -192     -27
3      -11      50      -5      20
 8     14
2      230      32     137      19
 9      1
1      226     -41     274     -50
3      286    -147     327    -169
5      269    -114     279    -118
7      165       4     167       4
 9      2
0     -174      -0    -174      -0
2     -479     119    -508     127
4       47     -32      62     -43
6      242     -15     259     -16
8      -90       8    -130      11
 9      3
1      436      57     487      63
3      334     184     326     180
5      241     130     223     120
7      151       8     163       9
 9      4
0       92      -0      48      -0
2     -172      34    -183      36
4     -275     -13    -248     -11
6      -73     -23     -69     -21
 9      5
1      578       4     573       4
3      357      78     383      84
5      152     115     166     125
7       65      44      63      43
 9      6
0     -474      -0    -495      -0
2      -46     -55     -55     -66
4      -43      83     -61     117
```

```
6      -154      112     -183      133
8        41       -1       72       -2
 9      7
1       279       44      237       37
3       210       46      262       57
5       206        5      199        5
7       111       37      114       38
 9      8
0      -255        0     -330        0
2       -73      107      -86      126
4       -44       88      -59      117
6       -47       17      -64       23
 9      9
1        52       20       65       25
3       134      -17      119      -15
5       185      -10      166       -9
7       121       -3      137       -3
 9      10
0       120        0      124        0
2      -151       68     -178       80
4      -147      -32     -136      -30
6         3      -19        6      -42
 9      11
1       206      -77      144      -54
3        97      -56       90      -52
5        78       -2       69       -2
 9      12
0      -161       -0     -183       -0
2      -163     -144     -132     -117
4         9       13        7       10
 9      13
1       184      101       94       52
3       146      155       94      100
 9      14
2        35       34       28       26
10      0
0       850        0      876        0
2       573     -317      589     -325
4       309     -379      312     -382
6       213      -48      209      -47
8       119       17      161       22
10      1
1       135      288      146      313
3      -188      -21     -194      -22
5       264       41      295       46
7       -83       68     -103       84
10      2
0       430       -0      464       -0
2       611      -97      589      -93
4       491      -27      456      -25
6       257      -85      250      -82
8       105      -33      142      -45
10      3
1       249      -23      259      -24
3       -46      268      -45      259
5       -18       56      -11       33
```

```
10      4
0       685        0      746        0
2       527      173      532      175
4       437       38      401       35
6       227      -51      237      -53
8        32      -58       33      -61
10      5
1        14       73       16       83
3       -59     -135      -70     -159
5       -59        2      -46        1
7       -17        1      -23        1
10      6
0       642        0      624        0
2       563      -96      543      -93
4       266       -8      263       -8
6       119      -32      114      -30
10      7
1      -414     -293     -395     -280
3       220     -109      225     -112
5       -77      -44      -97      -55
7        32      -22       72      -48
10      8
0       214        0      215        0
2       264      -26      221      -21
4       276      -43      284      -44
6       233       46      242       48
10      9
1        70      153       88      194
3      -169        8     -149        7
5        27      -59       42      -91
10      10
0       227       -0      165       -0
2       227       -5      231       -5
4       219      -10      190       -8
6       113      -37      141      -46
10      11
1       125      -91      111      -81
3       -19       73      -16       60
5        -2       17       -4       26
10      12
0       323        0      237        0
2       256       64      155       39
4       126        9      129        9
10      13
1        31       19       13        8
3        29      -61       29      -61
10      14
2       140       74      108       57
11      1
1       585       -9      615      -10
3       336       16      396       19
5        74       47      109       69
7        80       35      109       48
11      2
0       624       -0      622       -0
2    *  -26       33      -35       45
```

```
4      -79      -16      -81      -17
6       32       68       35       74
8      -88       14     -144       22
11      3
1       65       26      109       43
3      333       21      301       19
5      395      -49      382      -47
7      125      -48      155      -60
11      4
0      183       -0      222       -0
2       44       86       43       83
4      -66       12      -53       10
6      -12      -71       -9      -50
11      5
1      303      -52      320      -55
3      185     -125      158     -107
5      161     -144      181     -161
7      122      -66      138      -75
11      6
0     -447        0     -383        0
2       74     -195       81     -215
4      134     -148      130     -143
6      -65      -92      -61      -85
11      7
1      377      -58      322      -50
3      224      -74      235      -77
5      155       43      148       41
7       95       17      124       22
11      8
0      -52       -0      -79       -0
2       44      -95       50     -108
4       14     -112       15     -123
6      -14      -50      -19      -70
11      9
1      239       41      249       43
3      333      124      327      121
5      137       60      172       76
11     10
0      330       -0      302       -0
2        1       58        2       88
4      -80       33      -71       29
11     11
1      383       74      322       62
3      185       11      176       10
5       87      -35      110      -44
11     12
0       95        0       73        0
2       17      -28       28      -45
4       10        4       33       11
11     13
1      114     -115       69      -70
3      128      -37      124      -35
12      0
0      330        0      227        0
2      557      155      524      146
4       12      259       14      284
```

```
12      1
1      167      -24      166      -24
3     -278     -216     -285     -221
5       27      -52       50      -98
7       12       56       14       66
12      2
0      230        0      200        0
2       37      122       34      113
4      285      -32      256      -29
6      154      122      144      114
12      3
1       36      -80       34      -76
3     -180     -102     -187     -106
5       37      -52       47      -67
7       55      -26       56      -26
12      4
0      -32        0       -9        0
2      140     -239      113     -194
4      157      -36      121      -28
6      202      -80      221      -88
12      5
1      -26       91      -29      102
3      164       86      156       82
5       45       -8       55      -10
7      -21      -35      -25      -40
12      6
0      500       -0      474       -0
2      117       22      107       20
4      120     -135      118     -132
6      122       13      122       13
12      7
1       69      -52      109      -84
3      258       -4      288       -5
5      -67       30      -89       40
12      8
0       89       -0       61       -0
2      410      -13      391      -12
4      210      142      229      155
6       69       27       54       21
12      9
1      118       33      133       38
3      -90       11      -60        8
5       31       16       45       23
12     10
0      438        0      431        0
2      200      102      249      126
4      156      -37      163      -39
12     11
1       21      -49       10      -24
3      -81       -1      -52       -1
12     12
0      256        0      199        0
2      238     -152      196     -126
12     13
1      -56      -18      -17       -5
```

```
13     1
1       76     112      56      83
3      248     100     257     103
5      106     -10     105     -10
7      102     -34     118     -40
13     2
0      196      -0     190      -0
2     -158    -125    -163    -129
4      -42    -163     -51    -201
6      155     -11     196     -13
13     3
1      214     -65     242     -73
3      131     -41     140     -44
5      225     117     225     117
7       92      90     117     114
13     4
0      -89       0     -61       0
2      -11      53     -20      98
4      129      61     150      71
6      116      30     132      34
13     5
1      421      51     433      53
3       79     105      85     113
5      131      64     153      75
13     6
0       31      -0     127      -0
2      272      91     317     107
4       81     146      96     173
6      -73      40     -93      51
13     7
1      128      34     140      37
3      250      40     265      43
5      135      21     150      23
13     8
0      138      -0     175      -0
2      130      12     145      13
4       44      50      55      63
13     9
1       78     -25      79     -25
3      230     -45     227     -44
5       81     -30      84     -31
13    10
0      -23      -0     -47      -0
2      -52      15     -58      16
4       15       4      72      19
13    11
1      269      19     236      17
3       57     -15      44     -11
13    12
0      101       0      97       0
2        8     -35       5     -24
14     0
0      281      -0     215      -0
2      612     -48     620     -48
4      420     -54     496     -64
6      190    -154     214    -172
```

```
14     1
1      116     -25     116     -25
3        9      79      10      84
5        1     -47       1     -54
7  *     8       2      39       8
14     2
0      635      -0     657      -0
2      567     -89     536     -84
4      406    -125     417    -128
6      212       2     266       3
14     3
1       67     177      77     203
3      -74      19     -67      17
5      183      37     240      48
14     4
0      830       0     835       0
2      530      -7     514      -7
4      261      92     277      98
6      193      32     227      38
14     5
1      -32    -126     -30    -116
3      152     103     162     110
5      -44      82     -49      90
14     6
0      516       0     476       0
2      315     149     312     147
4      258       8     271       9
6      106     -16     204     -31
14     7
1       71      36     104      53
3  *     0       0       0     -47
5      -26       4     -42       7
14     8
0      -19      -0     -49      -0
2      256    -178     253    -176
4      239     -96     256    -103
14     9
1      -84     -36    -109     -48
3       57      54      72      69
14    10
0      180      -0     152      -0
2      121       9     103       8
14    11
1       69      97      65      92
15     1
1      455     -48     454     -48
3      464     -35     517     -39
5      177      -3     201      -3
15     2
0      196      -0     233      -0
2        8     196      10     226
4      -49      29     -29      17
6       -5     -16      -7     -20
15     3
1      497     -27     515     -28
3      292     -81     264     -74
```

```
5      227     -59     251     -65
15     4
0      -93       0     -85       0
2      -36     -46     -58     -74
4       25     -12      22     -10
15     5
1      304      90     298      88
3      138      70     126      64
5      212     -22     259     -27
15     6
0      -78       0    -106       0
2      -22     -82     -33    -121
4      -60     -33     -96     -52
15     7
1      177     -65     138     -51
3      211     -37     216     -38
15     8
0      -92       0     -86       0
2      -38       6     -33       5
4      -11     -28     -10     -26
15     9
1      103     -42      89     -36
3      146     -60     156     -64
15     10
0      -17       0     -15       0
2      -10      45     -11      47
16     0
0      239      -0     184      -0
2      270      21     256      20
4      201      86     201      86
16     1
1       50      42      57      48
3      -55      70     -50      64
5      -46     -27     -69     -40
16     2
0      224       0     161       0
2      324     -63     293     -56
4      127      44     108      37
16     3
3      -97     -73    -118     -89
5        7     -51      10     -74
16     4
0      344      -0     309      -0
2      -18      76     -21      92
4      152    -109     169    -121
16     5
1      -71    -113     -85    -136
3       42     -85      46     -94
5  *   -19      -2     -46      -6
16     6
0      104       0      80       0
2      173      -5     157      -4
4       74      79      93     100
16     7
1       16      41      21      55
```

```
16     8
0      202       0     240       0
2      177     -15     184     -16
16     9
1        1     -32       2     -53
17     1
1  *    14     -12      28     -23
3      178      54     216      65
17     2
0      113       0     106       0
2      -40      19     -55      26
4      -74     -36     -88     -42
17     3
1      206      66     208      67
3       41      29      39      28
17     4
0      -35      -0      -7      -0
2       19     -96      17     -82
4       14     -45      14     -45
17     5
1      131      23     157      27
3       67      20      59      18
17     6
0      -71      -0     -43      -0
2        9      54      11      70
17     7
1      158      -8     194     -10
17     8
0      -11       0     -32       0
18     0
0  *   -19      -0     -65      -0
2      215      -5     217      -5
4      203      35     255      44
18     1
1        3     107       3     107
3      -78      14     -95      17
18     2
0      204      -0     177      -0
2      202      14     215      15
18     3
1      -28     -32     -30     -34
3       -8      27     -17      54
18     4
0      337       0     397       0
2       82      27      58      19
18     5
1      -62      54     -71      62
18     6
0      103      -0      85      -0
19     1
1       31     -34      34     -38
19     2
0     -107       0    -139       0
2      -44      44     -71      71
19     3
1      118      33     159      44
```

APPENDIX II

List of |Fobs| and |Fcalc| for bis(dimethyldithiocarbamato) pyridine zinc. Scale absolute approx.

l	h	|Fobs|	|Fcalc|
0	2	206	223
	4	156	127
	6	252	245
	8	59	47
	10	21	29
	12	46	48
2	0	207	189
	2	55	15
	4	76	48
	6	76	46
	10	21	26
	12	46	63
	14	24	37
	-2	293	354
	-4	132	83
	-6	134	143
	-8	136	119
	-10	15	31
	-12	66	70
	-14	37	54
4	0	221	218
	2	21	49
	4	125	85
	6	197	223
	8	59	81
	10	68	88
	12	95	98
	16	13	6
	-2	187	131
	-4	32	101
	-6	114	94
	-8	19	33
	-10	37	42
6	0	317	274
	2	41	22
	4	143	140
	6	113	133
	8	37	42
	10	40	42
	12	23	28
	-2	167	192
	-4	110	107
	-6	214	242
	-8	115	116
	-10	20	23
	-12	27	27
	-14	19	24
8	0	13	11
	2	59	60
	6	70	93
	12	35	39
	-2	84	57
	-4	31	2
	-6	26	56
	-8	102	117
	-12	21	21
	-14	26	32
10	0	90	117
	4	136	146
	6	117	135
	8	22	24
	10	43	47
	12	44	30
	-2	65	82
12	0	44	64
	2	27	42
	4	72	73
	10	15	3
	-2	77	89
	-4	27	34
	-6	36	49
	-8	53	57
14	4	15	19
	6	15	20
	10	19	16
	-4	15	8
	-8	15	24
16	4	35	44
	-2	36	54
18	-2	16	28

APPENDIX III (a)

List of F_0, F_c for Bis(dimethyldithiocarbamato)pyridine Zn.½benzene.

* h k

(unobserved reflections in Appendix III(b))

ℓ	F_0	F_c
* 0	0	
2	-4165	-4908
4	1206	1366
E 6	7666	9162
8	-2428	-2500
10	-1825	-1813
12	-176	-452
14	-1147	-1108
16	-538	-537
20	-1219	-1001
24	519	536
* 1	0	
0	-3630	-4668
2	4722	5802
4	387	546
6	-3834	-4141
8	7071	7391
10	161	152
12	-1060	-761
14	2452	2433
16	-1151	-1066
18	1115	847
22	-952	-864
24	338	230
-2	-5245	-6104
-4	1777	1560
-6	-878	-710
E -8	-8535	-10691
-10	4147	4329
-12	-2323	-2095
-14	-2358	-2035
-16	2822	2677
-18	-805	-826
-20	1079	818
-22	997	818
-24	-827	-705
* 2	0	
0	-5019	-6324
2	-543	-317
4	4065	4109
6	-8016	-8800
8	-2162	-1908
10	-1084	-1106
12	-1566	-1341
14	-1841	-1674
16	589	326
18	1055	883
20	-623	-537
22	611	634
E -2	6234	8137
-4	1000	1319
-6	-3515	-3113
-8	5095	5349
-10	1492	1241
-12	-533	-496
-14	907	843
-16	-528	-507
-18	-1453	-1297
-22	-560	-524
-24	-1245	-1269
* 3	0	
0	6709	7454
2	514	69
4	176	573
6	6261	6668
10	-1817	-1749
12	2312	2244
16	-593	-568
18	-827	-562
20	413	343
22	-419	-374
E -2	7649	10886
-4	-4274	-5031
-6	-407	-306
-8	1975	2262
-10	-4431	-4558
-12	-836	-747
-14	345	359
-16	-2148	-2024
-18	2285	2385
-20	-228	-324
-22	-552	-440
-24	1441	1314
* 4	0	
0	775	703
2	-1692	-1607
4	-3531	-3677
6	-611	-572
8	1244	1045
10	1230	1250
12	-2665	-2563
14	2027	1872
16	1523	1279
18	-580	-521
20	1033	929
22	322	229
E -2	-6954	-7927
-4	-2756	-3007
-6	1426	1352
-8	-2747	-2619
-10	1007	909
-12	2328	2184
-16	1079	911
-18	1504	1484
-20	-1135	-1039
-22	679	625
-24	345	305
-26	-1293	-1505
* 5	0	
0	-1892	-1666
2	-1261	-1158
4	3344	3348
6	-4395	-4659
8	-1955	-1859
10	1593	1564
12	-2134	-2154
14	-593	-689
16	432	350
20	-647	-475
-2	1692	1611
-4	2602	2587
-6	-1829	-1704
-8	-682	-909
-10	1875	2032
-12	-1389	-1362
-18	-2320	-2306
-20	866	820
-22	-887	-690
-24	-765	-754
-26	407	364
* 6	0	
0	2797	2687
2	-3791	-3994
4	1684	1532
6	2466	2232
8	-493	-332
10	-1122	-1041
12	3051	3037
16	-910	-742
18	1754	1608
20	-567	-496
-2	659	747
-4	-3725	-3615
-6	1108	941
-8	-1920	-1930
-10	-1507	-1300
-12	1363	1387
-14	-466	-360
-16	1147	979
-18	1807	1649
-20	1591	1215
-22	330	306
-24	297	307
* 7	0	
0	-2872	-2658
2	2584	2766
4	-4031	-4193
6	-493	-415
8	2789	2580
10	-4127	-4293
12	548	365
14	1338	1112
16	-744	-693
-2	-1180	-1011
-4	907	914
-6	-1975	-2076
-8	785	854
-10	2510	2665

```
 -12     973     923
 -16    1931    1833
 -20   -1473   -1237
 -22     190     194
 -24    -567    -474
*  8       0
   0   -2678   -2441
   2    2476    2251
   4    1655    1519
   6   -2799   -2503
   8     737     733
  10    1661    1662
  12   -1509   -1385
  14    -438    -516
  16    1348    1194
  18   -1035    -963
  -2    1605    1607
  -4    1580    1430
  -6   -3222   -3279
  -8    2441    2060
 -10   -2433   -2301
 -12   -2126   -2029
 -14    2509    2464
 -16   -2487   -2538
 -20     352     329
 -24    -322    -221
*  9       0
   0    1315    1065
   2   -2662   -2671
   4     755     664
   6    1931    1937
   8   -2741   -2365
  10    1372    1160
  12     845     713
  14    -567    -468
  16     538     470
  -2     204     155
  -4   -2637   -2408
  -6    1667    1547
  -8   -1033    -937
 -12     878     751
 -14    1733    1651
 -16    -705    -690
 -18    1963    1756
 -20    1287    1199
 -22    -904    -763
 -24     881     877
* 10       0
   0    2079    2128
   2    -627    -400
   6     863     692
   8    -571    -464
  10   -1221   -1049
  14     190     211
  -2   -1327   -1254
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   -3    -669    -706
   -4     276     259
   -5     507     509
   -7     460     526
   -9    -620    -696
  -10     548     552
  -11     318     349
  -13     172     266
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  -16      92     200
 * 15     3
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   -3    -298    -225
   -5      92     227
   -7    -540    -616
   -9    -305    -358
  -10     225     226
  -11     298     389
  -12    -401    -446
  -13    -455    -663
 *  0     4
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    2    1830    1843
    3     376     134
    4     984     854
    5   -2085   -2063
    6   -2180   -2009
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    8    3281    3073
    9    1326    1324
   10    -381    -365
   11    -447    -483
   13    1042    1082
```

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   21    -507    -522
   22     345     375
   23    -306    -449
 *  1     4
    0    -568    -605
    1   -5007   -4664
    2   -2171   -1999
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    6    1477    1528
    7   -4838   -4330
    8   -1880   -1803
    9    1839    1770
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   13   -1089   -1192
   14   -1234   -1244
   15     637     687
   16     752     748
   19     889     744
   21     433     467
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   -3    4050    3855
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   -5    -697    -673
   -6    -996    -833
   -7   -2396   -2207
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   -9    5517    5072
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  -11    -474    -491
  -12     -98    -224
  -13     829     811
  -14     273     399
  -15    1885    1768
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  -17   -1124   -1116
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  -19     722     728
  -23    -647    -841
 *  2     4
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    1    -176    -198
    2     709     700
    3   -1466   -1331
    4    -546    -475
    5    5026    4534
    6     745     652
    7    -545    -522
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   17    -972    -917
   18     -92    -204
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   22    -322    -442
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   -5   -2252   -2332
   -6     -63     -79
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   -8   -1866   -1852
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  -11   -1599   -1625
  -12    -418    -502
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  -15    -657    -798
  -16    -421    -443
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  -22    -209    -240
  -23    -147    -197
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    9    1382    1351
   10    1221    1266
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   20     -90     -11
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  12     357     421
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  18     538     610
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  20    -359    -458
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  -7    -490    -416
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 -10   -1020   -1015
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 -12    -427    -424
 -13    -218    -305
 -14     111     178
 -15     156     281
 -16    -155    -343
 -17    -154    -282
 -18    -525    -490
 -19   -1246   -1293
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 -21     210     292
 -23    -349    -492
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   2     613     654
   3    -814    -911
   4    -498    -582
   5    3175    3171
   6    1331    1237
   7     367     372
   8     -80    -244
   9   -1294   -1464
  10    -552    -618
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  14    -595    -555
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  -2   -1159   -1038
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  -7   -1392   -1313
  -8    -921    -993
 -10    -897    -963
 -11   -1463   -1454
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 -13    -349    -444
 -14    -616    -761
 -15    -389    -417
 -16     -95    -318
 -17    -793    -841
 -18     779     753
 -19     985    1018
 -20    -513    -584
 -21     -75    -267
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   2     421     460
   3   -2188   -2263
   4    -206    -184
   5    -808    -824
   7    1448    1622
   8     853     908
  10     551     576
  11   -1533   -1660
  13    1158    1273
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  15     515     551
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  18    -328    -370
  -1    -737    -745
  -2   -1265   -1226
  -3   -2228   -2172
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  -6   -1106   -1149
  -7    -317    -245
  -8     643     574
  -9     972    1095
 -10    1162    1122
 -11     749     830
 -12    -962   -1086
 -14     317     437
 -15    1102    1085
 -16     272     352
 -17     650     716
 -22     304     383
 -23     214     283
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   0     799     776
   1   -1064   -1032
   2   -2007   -2005
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   4    1145    1279
   5   -1253   -1330
   6    -548    -577
   7    -982   -1143
   8    -956   -1120
   9    2237    2244
  10     466     525
  11   -1223   -1255
  12    -626    -535
  13    -743    -829
  14    -129    -264
  15     516     608
  16     195     244
  17    -200    -285
  -1     459     365
  -2     406     429
  -3    1393    1512
  -4    -775    -757
  -5    -480    -642
  -6     566     638
  -7     489     460
  -9     458     517
 -10     306     300
 -11    -545    -564
 -12    -792    -690
 -13    -391    -393
 -14     449     459
 -15     225     241
 -16    -409    -392
 -17   -1217   -1188
 -18    -494    -438
 -19    -519    -560
 -20     349     401
 -22    -250    -260
 -23    -327    -376
*   8      4
   0     886     979
   1   -1522   -1684
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     5     1381     1501
     6     -226     -347
     7     -806     -866
     8      413      344
     9      264       70
    10     -386     -416
    11     1335     1468
    13     -315     -374
    15     -312     -374
    16     -292     -432
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    -2     -482     -467
    -3    -1196    -1166
    -4     -663     -598
    -5    -1791    -1914
    -6     1748     1837
    -7     1346     1424
    -8    -1557    -1745
    -9    -2096    -2085
   -10      223      205
   -11     -277     -379
   -12      477      543
   -13     1321     1370
   -14     -225     -382
   -15    -1148    -1139
   -16       76       89
   -17      520      466
   -19      674      748
   -21      291      306
 *   9      4
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     1      527      705
     2      357      425
     3    -1830    -1788
     4     -155     -170
     6     -153     -302
     7     1048     1073
     8      760      730
     9    -1898    -1874
    10     -326     -347
    13      448      524
    14      207      202
    -2     1163     1113
    -3     -935    -1042
    -4     -352     -316
    -5     1604     1552
    -6      475      451
    -7     -503     -465
    -8      694      639
    -9      503      463
   -10      658      667
   -11     2187     2146
   -12      476      421
   -14     -486     -480
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   -15     -649     -701
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   -17     1570     1573
   -19     -501     -527
   -20     -394     -461
   -21     -680     -809
   -22      219      307
 *  10      4
     0     -501     -615
     1     1262     1255
     2      272      329
     3      514      573
     4     -264     -239
     5     -741     -739
     7      691      672
     8     -416     -489
     9      638      775
    11     -481     -579
    -1    -1251    -1322
    -2      615      704
    -3     1033     1177
    -4      227      325
    -6     -576     -596
    -7    -1232    -1294
    -8      897     1028
    -9     1235     1334
   -10     -224     -297
   -11     -641     -601
   -12     -404     -314
   -13    -1297    -1303
   -14      325      387
   -15     1140     1127
   -16     -465     -501
   -17     -798     -711
   -18     -117     -209
   -19     -605     -729
   -21      417      539
 *  11      4
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     2     -293     -326
     3      250      237
     6      253      265
     7     -546     -666
     9      420      449
    -2     -346     -430
    -3     -265     -233
    -4     -347     -374
    -5     -890     -953
    -6      490      572
    -7      306      387
    -9      607      653
   -10     -395     -557
   -11    -1019    -1051
   -12      354      371
   -13     1026     1061
```

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   -14      130      186
   -15      714      686
   -16     -174     -340
   -17     -931    -1044
   -18      148      268
   -19      960     1048
 *  12      4
     8      207      252
     9     -203     -309
    -1      540      522
    -2     -141     -382
    -4      497      539
    -5      381      427
    -7      892      835
    -8     -199     -229
    -9     -938     -978
   -10      868      941
   -11     1160     1160
   -12      129      227
   -13      175      368
   -14     -430     -494
   -15     -846     -944
   -16      464      553
   -17      208      306
   -18     -194     -240
   -19       89      173
 *  13      4
     0     -451     -430
     4      238      283
     6     -273     -412
    -2      625      666
    -3      279      327
    -4     -253     -252
    -5     -312     -260
    -6     -312     -289
    -7     -284     -348
    -8      307      392
    -9      118      127
   -10     -241     -293
   -11      117      186
   -12     -296     -317
   -13     -558     -594
 *  14      4
    -2      -90     -216
    -4     -148     -246
    -7      227      236
    -9      353      395
   -10     -299     -325
   -11     -337     -419
   -12      164      160
   -13      319      383
 *  15      4
    -5      416      570
    -7     -219     -265
```

APPENDIX III(b)

List of reflections too weak to be observed

Listed as: 100 h k

l $F_O(=\frac{1}{2}LpF_{min.})$ F_c

100	0	0
18	-337	-538
22	-275	-43
100	1	0
20	312	569
100	2	0
-20	328	252
100	3	0
8	-243	-370
14	326	201
100	4	0
-14	299	35
100	5	0
18	290	176
-14	-305	-216
-16	326	171
100	6	0
14	-333	-297
100	7	0
18	221	145
-14	-321	-112
-18	335	117
100	8	0
-18	-331	-372
-22	265	105
100	9	0
-10	-318	-228
100	10	0
4	337	4
12	265	2
-18	-308	-480
100	11	0
10	-265	-359
12	-216	-445
-8	-335	-669
-14	-330	-488
100	12	0
2	-325	-152
6	290	13
10	210	270
12	106	484
100	13	0
4	-273	-79
-10	-312	-184
100	14	0
-2	280	328
-14	243	21
-18	-158	-179

100	15	0
-8	-240	-89
-10	-231	-424
-12	213	298
-14	184	419
100	16	0
-4	-154	-80
-6	165	392
-10	-151	-276
100	1	1
12	-280	-198
15	-323	-26
18	-333	-91
20	-308	-209
-20	321	378
-21	-305	-17
100	0	1
6	-172	-86
10	-238	-453
18	-335	-219
100	2	1
16	333	612
17	-335	-63
18	-328	-525
22	236	159
24	-82	-191
-4	-147	-363
-6	-172	-337
-12	265	556
-18	-335	-608
-19	333	409
100	3	1
11	-290	-491
12	-303	-240
13	-316	-365
16	-335	-166
17	-330	-146
-5	-172	-112
-20	-326	-471
-21	-312	-683
100	4	1
15	-335	-101
16	-331	-274
22	-161	-226
-13	286	5
-19	-333	-439
-25	-184	-132

100	5	1
3	-226	-90
16	321	369
-7	223	501
100	6	1
16	305	237
-4	228	520
-23	-256	-53
-24	-221	-67
100	7	1
4	284	250
15	299	216
-21	-297	-68
100	8	1
13	-308	-382
14	291	161
15	267	370
-13	323	318
-17	333	27
-19	318	319
-21	284	399
100	9	1
11	-312	-182
12	-297	-75
13	278	387
-4	299	796
-14	335	552
-15	-335	-453
100	10	1
3	-333	-13
7	330	293
9	-312	-397
10	299	169
-8	-325	-92
-10	330	12
-21	-245	-371
100	11	1
6	318	192
11	238	50
-12	-333	-131
100	12	1
3	-316	-293
9	-231	-317
11	-168	-181
-13	316	127
100	13	1
4	-269	-164
-5	318	372

-11	303	438
-13	-290	-198
-14	280	41
-17	-236	-47
-19	184	100
100	14	1
1	252	57
5	-187	-141
-7	-284	-114
-11	267	122
-12	-261	-190
100	15	1
1	184	122
2	-165	-205
-1	-213	-58
-2	-221	-28
-3	-228	-15
-7	-236	-210
-11	-218	-248
100	0	2
6	175	425
19	-321	-504
20	305	120
100	1	2
16	-328	-194
17	-330	-141
22	238	75
-18	-330	-519
-19	-325	-236
-20	-312	-54
-23	-233	-12
100	2	2
19	-305	-493
-20	316	408
-22	-273	-353
100	3	2
10	-278	-63
-18	-330	-394
-20	316	82
-22	278	18
-24	-210	-125
100	4	2
17	312	382
-17	328	17
-23	-250	-10
-24	-213	-154
100	5	2
0	207	36
10	308	205
14	-330	-253
17	-293	-577
21	143	181
100	6	2
6	284	93
7	293	481
8	-305	-499

12	-330	-95
15	308	152
17	-267	-432
18	-238	-68
-25	143	6
100	7	2
0	261	357
8	321	393
10	-330	-148
16	-263	-82
19	135	27
-22	-259	-91
-24	190	149
100	8	2
3	303	548
8	330	86
10	-328	-229
12	-312	-421
14	278	202
16	223	407
-3	280	422
-15	-330	-389
-24	168	68
100	9	2
6	330	23
11	301	335
14	-238	-282
-6	305	457
-16	326	500
-17	319	258
-18	308	289
100	10	2
11	-267	-313
14	-181	-428
-8	-325	-550
-9	-326	400
-10	-328	-80
-11	330	120
-12	-330	-542
-14	328	201
-15	-323	-109
-17	305	7
-18	291	12
-19	275	490
-20	254	294
-21	228	64
-22	196	195
100	11	2
2	-328	-480
8	-282	-311
13	-135	-15
-9	330	331
-11	328	450
-13	-323	-324
-16	-299	-37

-17	286	544
-18	-269	-464
-19	-250	-339
-20	-226	-75
100	12	2
0	319	53
6	-271	-296
10	184	42
-14	-295	-623
-16	271	146
-21	139	195
100	13	2
8	-184	-197
-12	-295	-121
-16	-238	-204
-17	-213	-417
-18	184	104
-19	151	500
100	14	2
3	271	154
4	-250	-78
-8	328	210
-15	-238	-268
100	15	2
-4	216	328
-6	218	58
-11	-196	-102
-12	-187	-268
-13	-172	-275
-14	-147	-204
100	0	3
11	265	426
18	-316	-26
23	-187	-217
100	1	3
13	301	156
16	-321	-270
22	210	95
-10	-243	-730
-13	-290	-124
-15	-312	-121
-16	-319	-21
-22	-240	-69
100	2	3
14	-316	-400
16	-321	-639
19	284	625
-7	196	586
-14	301	346
-18	-319	-189
-20	297	421
-24	165	52
100	3	3
16	-316	-32
17	307	567
20	238	26

22	-139	-149
-16	319	49
-21	280	499
-22	252	199
-23	221	176
100	4	3
12	-316	-155
17	291	33
20	207	40
-7	-218	-248
-10	-254	-26
-18	-319	-456
100	5	3
14	-318	-651
15	307	460
16	-291	-122
17	-271	-368
18	-245	-99
-22	250	412
100	6	3
8	-307	-106
13	-316	-361
15	290	278
16	-269	-89
19	165	160
-24	165	54
100	7	3
6	-307	-144
12	-312	-216
18	-154	-301
-9	-286	-319
-10	291	833
-12	-307	-244
100	8	3
5	-314	-227
8	321	430
10	314	595
12	-291	-124
14	254	501
15	-226	-425
-18	-301	-146
100	9	3
10	295	251
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-18	-290	-232
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8	-293	-105
12	-218	-71
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-7	-319	-28
-13	-318	-8
-14	314	94
100	11	3
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6	-286	-12
7	273	544
8	259	504
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-18	245	8
-19	-223	-168
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4	273	221
10	135	98
-5	312	77
-9	307	409
-11	297	72
-14	273	163
-15	-263	-271
-18	-210	-294
100	13	3
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