A COMPARISON OF COPPER(I) AND COPPER(II) BOUND TO THIOETHER LIGANDS

A thesis presented in partial fulfilment
of the requirements for the
degree of M.Sc. in Chemistry at
MASSEY UNIVERSITY

GILLIAN E. NORRIS

1975.

Abstract

The structures of $Cu(II)(DTH)_2(BF_4)_2$ (where DTH = 2,5-dithiahexane) and $Cu(I)(DTO)_2BF_4$ (where DTO = 3,6-dithiaoctane) have been investigated by single crystal X-ray diffraction techniques. After full matrix least squares refinement of the structures, with anisotropic temperature factors for all non hydrogen atoms in the Cu(II) structure, and for all atoms larger than fluorine in the Cu(I) structure, the conventional R factor converged to a final value of 0.057 for the Cu(II) structure, and 0.082 for the Cu(I) complex.

The dark red crystals of the Cu(II) complex belong to the centrosymmetric monoclinic space group $P2_1/c$. with a = 8.082(3)Å, b = 10.282(3)Å, c = 11.893(4)Å and β = 115.3 degrees. Two dithiahexane ligands and two BF_4^- ions were found to co-ordinate to the Cu(II) ion to form a tetragonally distorted octahedron, with four Cu(II)-S bonds averaging 2.317Å in length, and two longer Cu(II)-F bonds averaging 2.576Å. The four sulphur atoms are part of two five membered Cu(II)-S-C-C-S rings in which both carbons are on the same side of the plane containing the copper and sulphur atoms.

The colourless crystals of the Cu(I) complex were obtained in the non-centric orthorhombic space group $Pna2_1$, with a = 14.581(2)Å, b = 13.421(2)Å and c = 10.781(2)Å. The molecules exist as discrete monomeric species, with no co-ordination of the BF_4^- ion to the metal ion. The two ligand molecules co-ordinate to the Cu(I) ion to form a distorted tetrahedron, with the S-Cu(I)-S angles varying between 94.0 and 121.1 degrees. The four Cu(I)-S bonds average 2.307Å in length, and hence are approximately equal to the Cu(II)-S bonds (within experimental error). The two five membered Cu(I)-S-C-C-S rings are both in a gauche conformation, with one carbon below the plane containing the Cu(I) and S atoms, and the other above. The BF_4^- ion was disordered and was refined using rigid group restrictions.

Cu-S co-ordination is thought to occur in some copper containing oxidation-reduction proteins. The observation of similar Cu-S bond distances when Cu(I) and Cu(II) are co-ordinated to thioether ligands (resembling the side

chain of the amino acid methionine) may therefore be of direct relevance to the copper co-ordination in such proteins.

ACKNOWLEDGEMENT

I would like to thank my supervisor, Dr. E.N. Baker, for his help and advice throughout this project. I would also like to thank Dr. E.W. Ainscough and Dr. A.M. Brodie for helpful discussions, Miss L.V. Kilengray and Mr. L. Pearson of the Massey University Computor Unit for their help with programs, and the many other people without whose help I could not have completed this project.

CONTENTS

CONTENTS

LIST OF FIGURES

CHAPTER I

INTRODUCTION

In biological systems metal ions are often found bound to proteins. Some of these proteins contain copper ions, and in many of these the copper is essential for their function. Most copper proteins are either involved in electron transfer (e.g. azurin, laccase), or the transfer of oxygen (e.g. haemocyanin). In the light of these functions, it is probable that the copper oscillates between its two oxidation states, viz. Cu(I) and Cu(II). In order to understand any structural changes associated with such oxidation-reduction processes, it is important to know and understand the co-ordination requirements of both Cu(I) and Cu(II). A similar knowledge of the co-ordination and steric requirements of iron, gained from the study of inorganic complexes, was very useful in synthesizing suitable model complexes to elucidate the oxygen binding mechanism in haemoglobin (1). Although extensive studies have been made on many copper proteins, no general conclusions have yet been reached about the nature of the ligands responsible for binding the copper, their stereochemistries, or indeed, the state of the copper itself. Hence, structural models for copper-protein interaction rely to a great extent on the co-ordination chemistry of low molecular weight complexes, since only one complete X-ray structural analysis of a copper protein has been achieved(49).

1. Probable Ligands for Copper Ions in Proteins

In proteins, the donor atoms available to act as ligands to copper ions are oxygen, nitrogen and sulphur. On the basis of the "hard/soft" classification given by Pearson (5,12,13), the type of ligands likely to bind to copper can be predicted. Thus Cu(I) preferentially binds to "soft" bases such as R_2S, RS^-, CN^- and CO because it is a "soft" acid. Cu(II), which is near the middle of the Pearson scale, preferentially binds to such bases as $-COO^-$, H_2O, OH^- and NH_3, but may also bind to "softer" ligands such as RS^-(5,13). In all metalloproteins whose structures have so far been determined, the metal ions are bound by the functional groups on amino acid side chains. Hence potential copper ligands will probably be

confined to those amino acids with suitable side chains. These can then be divided into those whose side chains are expected to prefer to bind to Cu(II), those that should prefer Cu(I), or those that may bind to Cu(II) and Cu(I)(5). To the first group belong serine and threonine, lysine, arginine, glutamic and aspartic acids, and histidine, having as their functional groups hydroxyl, amino, guanidino, carboxyl and imidazole groups respectively. The second, a much less investigated, group contains methionine and cysteine, which have thioether and sulphydryl groups as potential binding sites. From these two groups, the ligands most likely to bind to both Cu(I) and Cu(II) are histidine, methionine and cysteine (5,14). As electron transfer to and from copper in any "valence specific" environment would not be feasible under physiological conditions, suitable ligands in redox active copper co-ordination spheres are most likely to be imidazole, thioether and sulphydryl residues, these being ligands acceptable to both Cu(I) and Cu(II). It must be remembered, however, that in a protein a metal can be forced to accept a ligand it would not usually prefer under inorganic conditions, because a prepared site, depending on the protein structure, may be offered to it.

2. The State of Copper in Proteins

Copper atoms in proteins have been classified into three main types by Malkin and Malmström(2). These are, two paramagnetic forms, and one form which cannot be detected by electron paramagnetic resonance (E.P.R.).

Type I Copper

A characteristic property of this type of copper is the intense blue colour it imparts to proteins in which it is present. Spectrally, this is seen as an intense band in the visible region at about 600nm, with an extinction coefficient approximately one hundred times greater than that found for any low molecular weight copper complex. Since some proteins contain more than one atom of copper per molecule (e.g. ascorbate oxidase, which contains 8 atoms of copper per molecule), early theories predicted that such unusual spectra may be due to some sort of copper-copper interaction(3). It was then discovered that similar

spectra could be obtained from proteins with only one atom of copper per molecule (e.g. stellacyanin). It is now thought that such spectra may be caused by highly distorted ligand fields around the metal ion, which are forced on it by the protein(2,4,5). Unusual E.P.R. parameters also indicate that in blue proteins at least, the copper ion or ions are in an environment of low symmetry(2), which may be important for their function.

It has been suggested that the intense absorption for this type of copper, must be due to a very low energy charge transfer band(6), although it is difficult to decide whether the ground state is Cu(I)X or Cu(II)X^-. The energy of the transfer band means that the group X^- is strongly reducing relative to Cu(II), and the low energy of the d-d absorption bands leads to the conclusion that the site is of unusual geometry. Thus, the Cu(II) of "blue" proteins, may have an extremely reducing ligand such as -N= or $-S^-$. This has now been largely confirmed by N.M.R. and sequence studies which indicate that $-S^-$ is the most likely ligand(6).

Further evidence that the type I copper ligands include sulphur is presented by McMillin et al in two recent papers (7,8). These describe how the Co(II) derivatives of the "blue" proteins stellacyanin, plastocyanin and azurin were prepared and their spectra analyzed. As there was conclusive evidence that the Co(II) and Cu(II) metalloproteins were isomorphous, the spectra of the copper derivatives could be analyzed by reference to those of the cobalt derivatives, in which the bands were more easily interpreted. The results of such analyses strongly suggested that a sulphur ligand was bound to the metal, (Cu and Co), and that this ligand was probably of the type RS^- (i.e. from cysteine). Further evidence has recently been obtained from X-ray photo electron experiments which have established directly that sulphur is bound to copper in plastocyanin, and that the sulphur is most probably contributed by a cysteine residue in the protein(42).

Several explanations have been given for the high oxidation-reduction potentials found in proteins containing type I copper atoms, among which is the suggestion that

sulphur ligands are involved at the active site (2), and that at such sites, the Cu(I) state is favoured. As this state is favoured in non aqueous environments(4), an additional explanation has come from Österberg, who proposed that the "blue" copper sites must be situated in hydrophobic cavities in the proteins.

Type II Copper

This is referred to as "non blue" copper as it has spectroscopic and E.P.R. parameters similar to those found in low molecular weight Cu(II) complexes. It is often found in conjunction with "blue" copper in proteins which have oxidase activity. This may be because "non blue" Cu(II) has an unusual anion affinity, and hence may stabilize intermediates such as peroxide, which may be formed during the reduction of oxygen. It is usually thought to be bound to nitrogen ligands, as in the protein superoxide dismutase, where an X-ray structure determination has shown the copper to be bound to four histidine residues(49).

Type III Copper

In the non paramagnetic form either a cuprous ion(9) or a diamagnetic Cu(II)-Cu(II) pair, acting as a two electron accepting unit(2) is thought to be involved. The suspicion that sulphur ligands were involved in the binding of this type of copper in proteins dates from the investigations of Klotz et al on haemocyanin(10) in 1952. In 1958 they reported the species

$$\left[(Cu(I))_2(RS)_2 \longleftrightarrow (Cu(II)\ RS)_2\right]^{2+}$$

which was reinvestigated by Hemmerich in 1966(5). It was suggested that such a species might be a reasonable approximation to that found in natural systems. Beinert also suggested in 1966 that in cytochrome c oxidase, where there are two different types of copper, one E.P.R. detectable and one not, the latter type probably functions as an electron acceptor and may involve a disulphide system(11). Hemmerich then reported that the E.P.R. inactive copper of this protein became E.P.R. active in the presence of mercoptide blocking mercurials. Thus whether copper is present with a valency of one or two or some state intermediate between them an electron trans-

fer must be occurring within the protein, and binding to a disulphide group could provide a mechanism for this(5).

3. Copper Ion Interaction with Sulphur Ligand Atoms

As described above, spectroscopic studies strongly suggest that some of the copper atoms found in copper proteins have one or more sulphur ligands. Potential sulphur ligands present in proteins (thiols, thioethers, and disulphides) are already known to interact with iron(II) and iron(III). This has been shown by X-ray diffraction studies on single crystals of iron containing proteins and low molecular weight iron complexes(4,19). For example, the X-ray crystallographic structures of some ferrodoxins have shown that their active sites involve sulphur ligands from the thiol group of cysteine(20). Models of these oxidation-reduction proteins have been made by wrapping synthetic peptides of the type Cys-X-X-Cys (where X is an amino acid) around iron-sulphur cluster compounds of the type Fe_4S_4. In these complexes, the sulphur from the cysteine residues is bound to the iron atoms of the Fe-S clusters(4,5). Such complexes are found to have very similar spectra and redox potentials to the native proteins. The co-ordination of thioether groups is seen in the electron transfer protein cytochrome c. In this structure a thioether sulphur atom from methionine occupies the sixth co-ordination position of the iron atom(50). In both the iron proteins mentioned above the metal atom or cluster compound at the centre of the active site is bound to the apo-protein through at least one sulphur atom. Thus, it could be possible that the ligands which bind the metal to the protein play some role in its function of accepting or losing electrons. As the function of some copper proteins is very similar to that of these iron proteins (i.e. electron transfer or oxidation-reduction) the ligands offered to the copper ions by the proteins may be similar to those found in iron proteins, and hence involve some sulphur.

4. Small Molecule Studies of Copper Binding Sites

The structures of very few metalloproteins have so far been determined by X-ray crystallography. Even for those which have been, the accuracy of the data on the metal

co-ordination is limited in most cases by the relatively low resolution of the protein structure analysis. The study of small inorganic molecules, therefore, provides a means of obtaining very accurate data which may yield important information on aspects of the geometry of metal binding sites in metal-protein complexes. The studies of copper-peptide complexes by Freeman (15,16) have shown a variety of possible modes of co-ordination between copper atoms and amino acid ligands. However, these are mainly concerned with Cu(II) ions and oxygen and nitrogen ligands (e.g. amino and carboxyl groups) some of which would be involved in peptide bond formation in proteins and thus would probably not be available as ligands to metal ions.

Blue Cu(II) complexes in which the ligands are either four ammonia or four imidazole molecules have been reported (82) but although they have the colour characteristic of the "blue" copper proteins, its intensity is much less. A large number of crystal structures of Cu(II) complexes with nitrogen and oxygen ligands have been determined. In these complexes the ligand is usually found to be bound to the metal ion by a single covalent bond, the most common stereochemistries being square planar and octahedral (distorted)(4,79). Although simple complexes of Cu(II) and these ligands are known, chelated ones are generally found to be more stable, and hence are predominant(83). A number of compounds in which Cu(II) is bound to combinations of sulphur and nitrogen ligands (e.g. thiosemi-carbazides) have also been investigated(17,18) and although few of the ligands are closely comparable with those available in proteins, they can give valuable information about the type of bonding possible between Cu(II), and sulphur and nitrogen.

Most of the Cu(I) crystal structures investigated so far contain ligands such as acetonitrile, chloride, bromide and iodide, which are far removed from the sort of ligands available in proteins. However, Österberg has reported some Cu(I)-imidazole structures(4) which can be compared with very similar Cu(II) complexes. X-ray diffraction studies have been carried out on Cu(I)-thiourea chloride and other similar complexes(78), but only a single Cu(II) structure of this kind is known, viz. that of Cu(II)-

tetramethylthiourea chloride (34). Other structures which may have biological significance are those of the Cu(I) thiocarbamates, which form cluster compounds(17). These can be compared with similar Cu(II) clusters, and are interesting because in some copper proteins (e.g. ceruloplasmin), there is more than one copper atom per molecule and clusters could occur. Complexes in which both sulphur and nitrogen are co-ordinated to Cu(I) ions have been reviewed, together with the similar co-ordination complexes of Cu(II) ions (17,18). The former complexes are invariably tetrahedral, although the tetrahedra may be distorted(71), and may involve some $p\pi$ or $d\pi$ bonding between the Cu(I) ion and the ligands(79).

In general, however, ligands containing sulphur as a donor atom to copper ions have been much less studied than those containing oxygen and nitrogen. In particular, few complexes have been prepared involving sulphur ligands similar to the potential ligands available in proteins. Thioether ligands such as dithiahexane (DTH), and dithiaoctane (DTO), appear to offer excellent opportunities to study the interaction of copper ions with a sulphur ligand closely resembling one of those likely to bind copper in proteins. This is because DTH and DTO are very similar to the side chain of the amino acid methionine.

Methionine $CH_3-S-CH_2-CH_2-\underset{\displaystyle H}{\overset{\displaystyle NH_2}{C}}-COOH$

DTH $CH_3-S-CH_2-CH_2-S-CH_3$

DTO $CH_3-CH_2-S-CH_2-CH_2-S-CH_2-CH_3$

In addition, it was shown by Bergen(21) that both Cu(I) and Cu(II) complexes with DTH ligands could be prepared. It was the aim of this project, therefore, to determine the structures of a Cu(I) and a Cu(II) complex with the same ligand system, in order to compare differences between them. As copper proteins are involved in redox processes, a binding site for the copper ion which does not change ligand geometry drastically during the uptake or loss of one electron would be expected(14). Changes in bond length, or in the type of bonding, or small changes in geometry, may however be crucially important in the function of such

proteins. Although it is unlikely that the geometry around the metal ion in these proteins could be simulated, such a study may be of considerable help in further understanding about bond lengths and bond types between copper ions and proteins.

CHAPTER II

PRELIMINARY INVESTIGATIONS

1. Crystallisation

$Cu(II)(DTH)_2BF_4)_2$ and $Cu(I)(DTH)_2BF_4$ were prepared and characterised by Bergen(21). $Cu(II)(DTH)_2(BF_4)_2$ was recrystallised by evaporation from acetone, and $Cu(I)(DTH)_2BF_4$ was recrystallised from a 7:3:1 mixture of acetone, chloroform and methanol, by the same method. The $Cu(II)(DTH)_2(BF_4)_2$ crystals were dark red in colour and needle shaped, and the $Cu(I)(DTH)_2BF_4$ crystals were cream in colour and were obtained mainly as fragments of crystalline aggregates. $Cu(I)(DTO)_2BF_4$ crystals were prepared by Palmer(22) and were long thin colourless needles. Crystals which completely extinguished under polarized light, and which appeared to be single and well formed, were mounted on glass fibres using a quick setting adhesive, and then sealed in glass capillary tubes.

2. Determination of the Unit Cell Parameters

The density of all the crystals examined was measured by flotation in a hexane-iodomethane mixture. From the density, the number of molecules of each compound in its respective unit cell could be calculated using the formula

$$n = \frac{\rho NV}{M}$$

where V is the volume of the unit cell

ρ is the density of the crystal

N is Avogardro's Number

M is the molecular weight of the compound.

Oscillation, Weissenberg and Precession photographs were taken on a Phillips 1130/00 X-ray generator using nickel filtered CuKα radiation. Results were as follows:

(a) $Cu(II)(DTH)_2(BF_4)_2$

Oscillation and Weissenberg photographs showed the crystals to be monoclinic, with hol reflections systematically absent when $l = 2n + 1$ and oko reflections systematically absent when $k = 2n + 1$. The space group was therefore uniquely defined as the centrosymmetric space group $P2_1/c$. The distance between the layer lines on the oscillation photographs, and between the spots along the axes of the Weissenberg photographs, gave unit cell

dimensions of a = 8.096Å, b = 10.425Å and c = 11.812Å. β was measured from the separation of the axes on the hol photograph and was found to be 115.2 degrees. The density of the crystals was measured as 1.8 gm/cm^3, and assuming a molecular weight of 481.4, the number of molecules per unit cell was calculated to be 2.

(b) $Cu(I)(DTH)_2BF_4$

The Weissenberg photographs of the crystal showed an axial repeat every 30mm (60 degrees). Confirmation that this higher symmetry did exist was sought by taking oscillation photographs at steps of 60 degrees from the original position, through 360 degrees. It was found that photographs taken at intervals of 120 degrees were identical, showing the crystal to be mounted along a three fold axis. Precession photographs were then taken to aid further identification of the space group, which was subsequently found to be a rhombohedral lattice based on a hexagonal reference system (rhombohedral inverse). Systematic absences in the hkl reflections were found when $-h + k + l = 3n + 1$ or 2, and in the hol reflections when $h + l = 3n + 1$ or 2, and when $l = 2n + 1$, indicating that the crystal belonged to the space group $R\bar{3}c$. The cell constants calculated were a = b = 24.565Å, c = 14.99Å, $\alpha = \beta = 90$ degrees, $\gamma = 120$ degrees, $\rho = 1.56$ gm/cm^3, n = 18.

(c) $CU(I)(DTO)_2BF_4$

Oscillation, Weissenberg and Precession photographs showed the crystals to have orthorhombic symmetry. Reflections okl were systematically absent for $k + l = 2n + 1$, and hko reflections were absent when $h = 2n + 1$, indicating the space groups $Pna2_1$ or Pnma. The cell constants calculated were a = 14.88Å, b = 13.42Å, c = 10.76Å, $\alpha = \beta = \gamma = 90$ degrees, $\rho = 1.405$ gm/cm^3, n = 4.

Since the space groups $Pna2_1$ and Pnma belong to the point groups mm2 and mmm respectively, the number of asymmetric units per unit cell may suggest the proper choice of space group. The number of molecules per unit cell was calculated to be 4, the number of asymmetric units given for the point group mm2, whereas the number for the point group mmm is 8. As a unit cell can contain fewer molecules than asymmetric units only if the molecules possess one or

more of the point symmetry elements which appear in the space group, and can position themselves in the cell so that the corresponding elements coincide, it was thought that the proper choice of space group was $Pna2_1$. This was because Pnma is a centrosymmetric space group, and would therefore require the molecules to contain a centre of symmetry. The usual stereochemistry of Cu(I) complexes of this type is tetrahedral, and the molecules are therefore unlikely to be centrosymmetric.

3. Choice of Crystals for Structure Determination

It was the original aim of this thesis to compare the structures of a Cu(II) complex and a Cu(I) complex with exactly the same ligand system in each. Only one Cu(II) thioether complex was available, that of $Cu(II)(DTH)_2(BF_4)_2$. The corresponding Cu(I) complex, $Cu(I)(DTH)_2BF_4$, could only be obtained as aggregates of crystals, from which it was virtually impossible to obtain single fragments suitable for structure analysis. It was therefore decided to determine the structure of the closely related Cu(I) complex $Cu(I)(DTO)_2BF_4$, which differs only in the substitution of ethyl groups for the methyl substituents on the sulphur atoms of the ligand. The formula and numbering systems for these two molecules are shown in Figures 1, 6 and 7.

CHAPTER III

STRUCTURE DETERMINATION FOR $Cu(II)(DTH)_2(BF_4)_2$

1. Data Collection

Intensity measurements were made on a Hilger and Watts four circle diffractometer controlled by a P.D.P. 8/I computer, using MoKα radiation (λ = 0.7017Å). The crystal was mounted along its needle axis (b) and the 2θ, ω, ϕ and settings were determined using twelve strong reflections which were well dispersed in reciprocal space. These values were used in a least squares refinement of the cell parameters and orientation matrix. The resulting cell parameters were a = 8.082(3)Å, b = 10.282Å, c = 11.893(4)Å, α = 90.0 degrees, β = 115.3 degrees, γ = 90.0 degrees, where the standard deviation in the least significant figure is given in parentheses following each parameter. Intensities were measured by a 2θ-ω scan through each reflection, consisting of 50 steps of 0.02 degrees, each lasting one second. Background counts were taken for 10 seconds at the beginning and end of each scan. Three standard reflections, 0 0 6, 0 6 0, 7 0 -2, were measured after each batch of 50 reflections, to check for crystal damage, misalignment and the general working precision of the apparatus. Reflections measured were of the type hkl, $hk\bar{l}$, $h\bar{k}l$ and $h\bar{k}\bar{l}$, each being measured once, and the measurements being taken up to an angle of θ = 25 degrees. This gave a total of 3840 reflections.

2. Data Reduction

Integrated intensities were calculated by the computer program HILGOUT(81) using the relationship

Intensity = Scan-$(BG_1 + BG_2)$ * TSCL.

Where Scan = the total count for the step scan

BG_1 = the first background count

BG_2 = the second background count

TSCL = the ratio of the peak to background counting times

= 2.5

Standard deviations were calculated for each reflection using the equation

$$\sigma I_{hkl} = \left[\text{Scan} + (BG_1 + BG_2)*TSCL^2 + (FSIG \times I_{hkl})^2\right]^{1/2}$$

where FSIG was given the value 0.05.

The data were then corrected for Lorentz and Polarization effects in the usual way(23). For MoKα radiation, the linear absorption coefficient for $Cu(II)(DTH)_2(BF_4)_2$ is $\mu_\lambda = 17.99cm^{-1}$. The dimensions of the crystal used in the data collection were 0.7 x 0.4 x 0.3 mm, so that the cylindrical absorption factors over the range of sin θ values in the data collection ranged from 3.16 to 2.48. Because of the difficulties in allowing for absorption by the capillary tube, and because this range of absorption factors was not considered too great, no correction was made for absorption.

Except for the reflections systematically absent, all data were retained, none being rejected as "not significantly above background". The maximum variation in the intensities of the standard reflections over the whole data collection was less than 3σ, and no decay corrections were therefore applied. Equivalent reflections were averaged to give a final data set of 1584 reflections. Of these 234 were less than σ, 108 were between σ and 2σ, 92 were between 2σ and 3σ, and 1146 were greater than 3σ.

3. Structure Determination

Atomic scattering factors for Cu, S, C, F, B and H were taken from the "International Tables for X-ray Crystallography"(24). For copper, the values were corrected for anomalous dispersion using values from the same source. All calculations were carried out on a Burroughs B6700 computer.

The equivalent positions for the space group $P2_1/c$ are (I) x,y,z; (II) $\bar{x},\bar{y},\bar{z}$; (III) $\bar{x}$,1/2-y,1/2+z; (IV) x,1/2 + y, 1/2 - z. As the number of molecules in the unit cell had been found to be 2, the copper atom was assigned to a centre of symmetry at (0,0,0). The position of the copper atom was used to give an estimate of the phase of each reflection using the equivalent tan α = B/A.

Where $$B = \sum_j f_j \sin 2\pi(hx_j + ky_j + lz_j)$$

$$A = \sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j)$$

and $$F = A + iB.$$

When a crystal has a centrosymmetric structure and the symmetry centre is chosen as the origin of coordinates, then for every atom at a point xyz there is another at

$\overline{xyz}$. Thus B = 0 because sin (-x) = -sin x, and the sine terms sum to zero in pairs.

$$\therefore F_{hkl} = 2 \sum_{j=1}^{J/2} f_j \cos 2\pi(hx_j + ky_j + lz_j)$$

$$\tan \alpha = \tan 0$$

$$\therefore \alpha_{hkl} = \tan^{-1} 0 = 0 \text{ or } \pi.$$

Only reflections with k + l = 2n were used in the calculations because the copper atom, as a result of its special position, contributes to these alone.

An electron density map was then calculated by the computer program FOURIER(25) using the expression

$$= \frac{1}{V} \sum_h \sum_k \sum_l |F_{hkl}| \exp i\alpha \exp - 2\pi i (hx + ky + lz)$$

where the $|F_{hkl}|$ values were the measured amplitudes, and the phases α were those of the copper atom contribution. The resulting electron density map showed strong peaks for the sulphur atoms. These were then included in the phase determination and a further electron density map was calculated using the new phases. Isotropic temperature factors were introduced for each atom to account for the thermal motion. The remaining atoms were identified from electron density maps by assuming approximate bond lengths and angles as follows: S-C, 1.81Å; C-C, 1.54Å; Cu-F, 2.1Å; B-F, 1.54Å; C-H, 1.08Å; F-B-F, 109 degrees; S-C-S, 109 degrees; F-Cu-S, 90 degrees(31). Thus the positions of the 4 carbon atoms and 1 of the fluorines were determined from the map phased by the copper and two sulphur atoms, and a further map then revealed the positions of the remaining three fluorine atoms, and the boron atom. No other large peaks remained unaccounted for.

4. Refinement of the Structure

The structure was refined by minimising $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ is the observed structure factor magnitude, and $|F_c|$ is the calculated structure factor magnitude, using the full matrix least squares program CUCLS(26). The weight w was estimated from the standard deviations in each measurement using the relationship

$$w = 4|F|^2/\sigma^2 \quad (|F|^2)$$

A total of 1238 reflections with $|F_o|^2 > 2\sigma|F_o|^2$ were used in the refinement. The conventional R factor or residual

index R, is given by

$$R = \frac{\sum (|F_o| - k |F_c|)}{\sum |F_o|}$$

where k is the scale factor used for the data. This function was used to indicate the degree of agreement between the observed and calculated structure factors. A weighted R factor was also calculated using the relationship

$$R_w = \sqrt{\frac{\sum w(|F_o| - k |F_c|)^2}{\sum w(|F_o|^2)}}$$

The estimated standard deviation or error E in an observation assigned unit weight was given by

$$E = \sqrt{\frac{\sum w(|F_o| - k|F_c|)^2}{NO - NV}}$$

where NO = the number of reflections or observations
NV = the number of variables or parameters refined.

The weighted R factor or the error E were taken as being better indicators of convergence than the conventional R factor, R, which is not a function of the weighting of the data.

Three cycles of least squares refinement in which isotropic temperature factors were used for all atoms reduced R from 0.278 to 0.138. Anisotropic temperature factors were then calculated for all atoms, but because of the limit on the number of parameters which could be refined simultaneously, each complete cycle of refinement had to be done in two alternate blocks. Thus, the Cu(II) DTH atoms were refined as one block, followed by the BF_4 atoms as the other. After two cycles of refinement, the positional and thermal parameters of the Cu, S and C atoms converged, further refinement of them having little effect on the R factor. However, the positions of the atoms of the BF_4 group tended to oscillate, perhaps because of high thermal parameters or some degree of disorder, so that 9 cycles of refinement of these atoms were required to bring about a convergence of the R factor at 0.067. During this refinement, several difference Fourier maps were calculated to check the positions of the atoms in the group. A final least squares cycle of the Cu(II) DTH atoms brought the R factor to 0.064 and the weighted R factor to 0.090. The hydrogen atoms were then located from a difference Fourier map and inclusion

of these positions in the structure factor calculation reduced the R factor to 0.057 and the weighted R factor to 0.080. The hydrogen atom parameters were not refined because of the small number of data, and were thus designated B values approximately 1.2 times those of the carbon atom to which they were attached(64). The final standard error in an observation of unit weight for this structure was 1.7846 electrons. A final difference Fourier was then calculated, the principal features of which are shown in Table I.

Peaks 1-5 are in the immediate vicinity of the BF_4 atoms, and presumably reflect the inadequate treatment of thermal motion or disorder, in the BF_4 group. The trough (peak 5) is very near one of the fluorines (0.4301, 0.2737, -0.1766). However, difference syntheses can return correctly placed atoms in holes which have minima of approximately $1 e/A^3$(23) for a variety of reasons. One of the most common of these is the use of temperature factors which are too small. This has the effect of increasing the calculated peak density above its true value. That these features are signs of disorder in this group of atoms is suggested by their large amplitudes of vibration, particularly along the z axis (Table IV). Similar amplitudes of vibration have previously been found for the atoms of free BF_4^- ions (63). Peaks 6 and 7, and 8 and 9, are all in the vicinity of C(6) and C(7) and may reflect some disorder in this part of the DTH ligand.

TABLE I - PRINCIPAL FEATURES OF FINAL DIFFERENCE FOURIER

Peak Number	x/a	y/b	z/c	$e.A^{-3}$
1	-0.2019	0.2994	-0.1791	1.066
2	-0.1584	0.2354	0.0033	0.924
3	-0.3273	0.3261	-0.2108	0.825
4	0.3975	0.2702	-0.0728	0.731
5	-0.4198	0.3022	-0.1721	-1.573
6	-0.0366	-0.0651	0.2522	0.853
7	-0.0749	-0.0040	0.2444	-1.629
8	-0.3260	0.0036	0.1299	-1.047
9	-0.1096	0.0566	0.2166	0.876

It was noted that the C-C bond was in fact shorter than expected (1.37Å) and that when a plane was calculated through the Cu(II) atom and the two sulphur atoms of one ligand, both of the bridging carbon atoms were on the same side of

the plane. As this was unexpected (see description of the structure), and as there was a suggestion of some disorder about C(6) and C(7) in the final difference Fourier, a disorder model was introduced in which C(6) and C(7) were each treated as two half atoms approximately 0.7Å apart (48), (see Figure 3). Three cycles of least squares refinement of this model, in which x, y, z and B were varied gave final values of R = 0.059, R_w = 0.080 and E = 1.8017 electrons. The R factor and Standard Error for this model are thus slightly higher than for the unmodified structure /0.059 cf. 0.057; 1.8017 cf. 1.7846/, although the weighted R factors are the same in both cases. These values indicate that the bond lengths for the disorder model after refinement are probably less reliable than the original ones.

The final fractional co-ordinates and isotropic temperature factors for the atoms involved in the disorder model are shown in Table II. The numbering system is the same as that shown in Figure 3, and the standard deviation in the least significant figure is given in parentheses following each parameter.

TABLE II - FINAL FRACTIONAL CO-ORDINATES OF THE DISORDER MODEL

Atom	Occupancy	x/a	y/b	z/c	B(Å²)
C-VI	0.5	-0.076(4)	0.005(2)	0.241(3)	8.0(6)
C-VII	0.5	-0.056(1)	-0.065(1)	0.245(1)	2.2(2)
C-VIII	0.5	-0.218(3)	-0.074(2)	0.165(2)	7.0(4)
C-IX	0.5	-0.259(2)	-0.027(2)	0.148(2)	3.7(3)

Observed and calculated structure factors have been tabulated (Appendix 1). The final fractional co-ordinates and anisotropic and isotropic temperature factors of the atoms not related by a centre of symmetry are shown in Tables III and IV. The numbering system corresponds to that shown in Figure 1, apart from the hydrogen atoms which are numbered consecutively, as well as according to the carbon atom to which they are attached.

TABLE III

FRACTIONAL CO-ORDINATES OF NON CENTROSYMMETRICALLY RELATED ATOMS OF $Cu(II)(DTH)_2(BF_4)_2$

ATOM		x/a	y/b	z/c	B(a)
Cu	1	0.0000	0.0000	0.0000	
S	2	0.0883 (2)	0.0596 (2)	0.2056 (1)	
S	3	-0.2770 (2)	-0.0677 (2)	-0.0053 (2)	
C	4	0.304 (1)	-0.0139 (7)	0.2992 (6)	
C	5	-0.286 (1)	-0.2419 (7)	-0.0233 (8)	
C	6	-0.064 (1)	-0.046 (1)	0.2418 (8)	
C	7	-0.243 (1)	-0.043 (1)	0.1541 (8)	
F	8	-0.2361 (8)	0.4258 (4)	-0.0581 (5)	
F	9	-0.1331 (7)	0.2263 (5)	-0.0834 (6)	
F	10	-0.4293 (8)	0.2742 (6)	-0.1770 (6)	
F	11	-0.291 (1)	0.2483 (6)	0.0227 (7)	
B	12	-0.274 (1)	0.2982 (8)	-0.0800 (8)	
H	5	-0.290	-0.260	-0.100	6.6
H	5	-0.390	-0.277	-0.027	6.6
H	5	-0.170	-0.2813	0.0355	6.6
H	7	-0.330	-0.1146	0.160	10.0
H	7	-0.275	0.0417	0.1552	10.0
H	6	-0.040	-0.0156	0.334	10.0
H	6	-0.020	-0.135	0.240	10.0
H	4	0.290	-0.110	0.286	7.6
H	4	0.330	0.000	0.3784	7.6
H	4	0.380	-0.0156	0.2073	7.6

(a) Isotropic temperature factors are of the form $\exp[-B(\sin^2\theta)/\lambda^2]$ where $B = 8\pi^2\mu^2$, and μ^2 is the mean square amplitude of vibration. Temperature factors of all non hydrogen atoms are shown in Table IV.

TABLE IV

THE ANISOTROPIC TEMPERATURE FACTORS[a] AND R.M.S. AMPLITUDES OF VIBRATION[b] FOR ALL NON/HYDROGEN ATOMS

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	μ_x	μ_y	μ_z
Cu	0.0134(2)	0.0079(1)	0.0062(1)	0.0008(1)	0.0042(1)	0.0003(1)	0.1791	0.1915	0.2095
S	0.0187(3)	0.0114(2)	0.0076(1)	-0.0000(2)	0.0053(2)	-0.0015(2)	0.1998	0.2244	0.2542
S	0.0157(3)	0.0121(2)	0.0087(2)	-0.0016(2)	0.0057(2)	0.0006(1)	0.1922	0.2242	0.2601
C	0.020 (1)	0.0131(8)	0.0077(6)	0.000 (1)	0.0039(7)	0.0003(6)	0.2105	0.2458	0.2669
C	0.025 (2)	0.0102(8)	0.0146(9)	-0.005 (1)	0.008 (1)	0.0006(7)	0.1943	0.2757	0.3048
C	0.024 (2)	0.043 (2)	0.0096(7)	-0.008 (2)	0.010 (1)	0.001 (1)	0.1813	0.2743	0.4873
C	0.034 (2)	0.029 (2)	0.0106(8)	-0.014 (2)	0.011 (1)	-0.003 (1)	0.2191	0.2571	0.4218
F	0.040 (1)	0.0109(5)	0.0173(6)	-0.0012(7)	0.0156(8)	-0.0009(5)	0.2415	0.2729	0.3420
F	0.022 (1)	0.0187(6)	0.0239(8)	0.0016(7)	0.0092(7)	-0.0068(7)	0.2211	0.2810	0.4123
F	0.028 (1)	0.0230(8)	0.0230(7)	0.0067(9)	-0.0044(9)	-0.0093(7)	0.2354	0.2870	0.5019
F	0.088 (3)	0.0183(8)	0.027 (1)	-0.003 (1)	0.036 (2)	0.0005(8)	0.2670	0.3206	0.5020
B	0.016 (1)	0.0103(8)	0.0105(7)	-0.001 (1)	0.0059(9)	-0.0028(7)	0.2036	0.2070	0.2703

(a) The anisotropic thermal parameters are of the form

$$\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$$

(b) These values correspond to the root mean square amplitudes of vibration in Angströms of the atom along the three principal axes of its vibration ellipsoid.

(c) The standard deviation in the least significant figure is given in parentheses following each parameter.

5. Description of the Structure

In this complex the asymmetric unit comprises one half of the molecule, the copper atom being situated on a centre of symmetry. Thus, the two halves of the molecule are related and must be identical. Interatomic distances and angles (with standard deviations) are shown in Tables V and VI, and the overall geometry of the molecule is shown in Figure 1. The molecules are monomeric, and are separated by normal van der Waal's distances, with no abnormally short intermolecular contacts. The arrangement of molecules in the unit cell is shown in Figure 2.

The Cu(II) ion is octahedrally surrounded by six ligands consisting of four sulphur atoms from the two DTH molecules, and two fluorine atoms from the two BF_4^- groups. Because of the restrictions imposed on the symmetry of the molecule by the space group, the copper atom and the four sulphur atoms are necessarily co-planar. The Cu(II)-S bonds are 2.315 ± 0.002Å and 2.319 ± 0.002Å in length, and the Cu(II)-F bond is 2.580 ± 0.002Å long, so that the octahedron is tetragonally distorted.

When the ligands are mainly σ bonding (e.g. sulphur) the preferred stereochemistry of the Cu(II) ion is octahedral rather than square planar. However, because it is d^9, its geometry should be distorted from normal octahedral symmetry due to a combination of the Jahn-Teller and Pauling Electroneutrality effects (32). The static form of this distortion is usually a tetragonally distorted octahedron(32), and, in such complexes involving monodentate ligands, the axial fifth and sixth ligands are often bonded at a distance approximately 0.6Å greater than the bonded distance of equatorial ligands. The Cu(II) ion can thus be considered ellipsoidal rather than spherical, its in plane radius being approximately 1.3Å and its out of plane radius being approximately 1.9Å, depending on the degree of tetragonal distortion (32). Using these values for the covalent radii of the Cu(II) ion, and assuming covalent radii of 1.04Å for sulphur and 0.64Å for fluorine(31), the predicted Cu(II)-S and Cu(II)-F single bond lengths for a tetragonally distorted structure are about 2.34 and 2.54Å respectively. These values are very similar to those found in the structure determination (2.317 and 2.580Å respectively). A similar stereochemistry has been

FIG.1 010 projection of the Cu. $(DTH)_2(BF_4)_2$ molecule

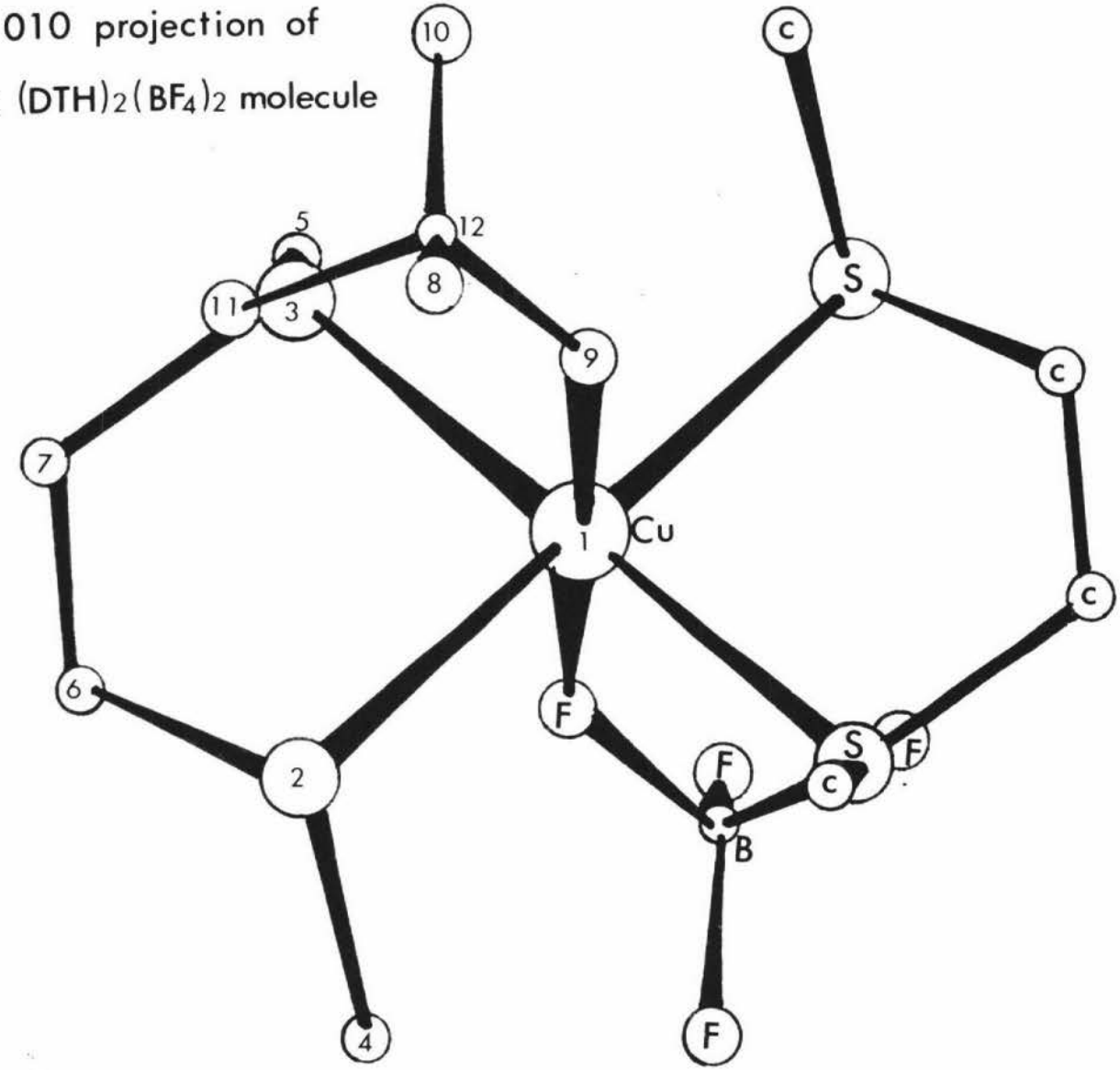

FIG. 2 001 projection of the unit cell

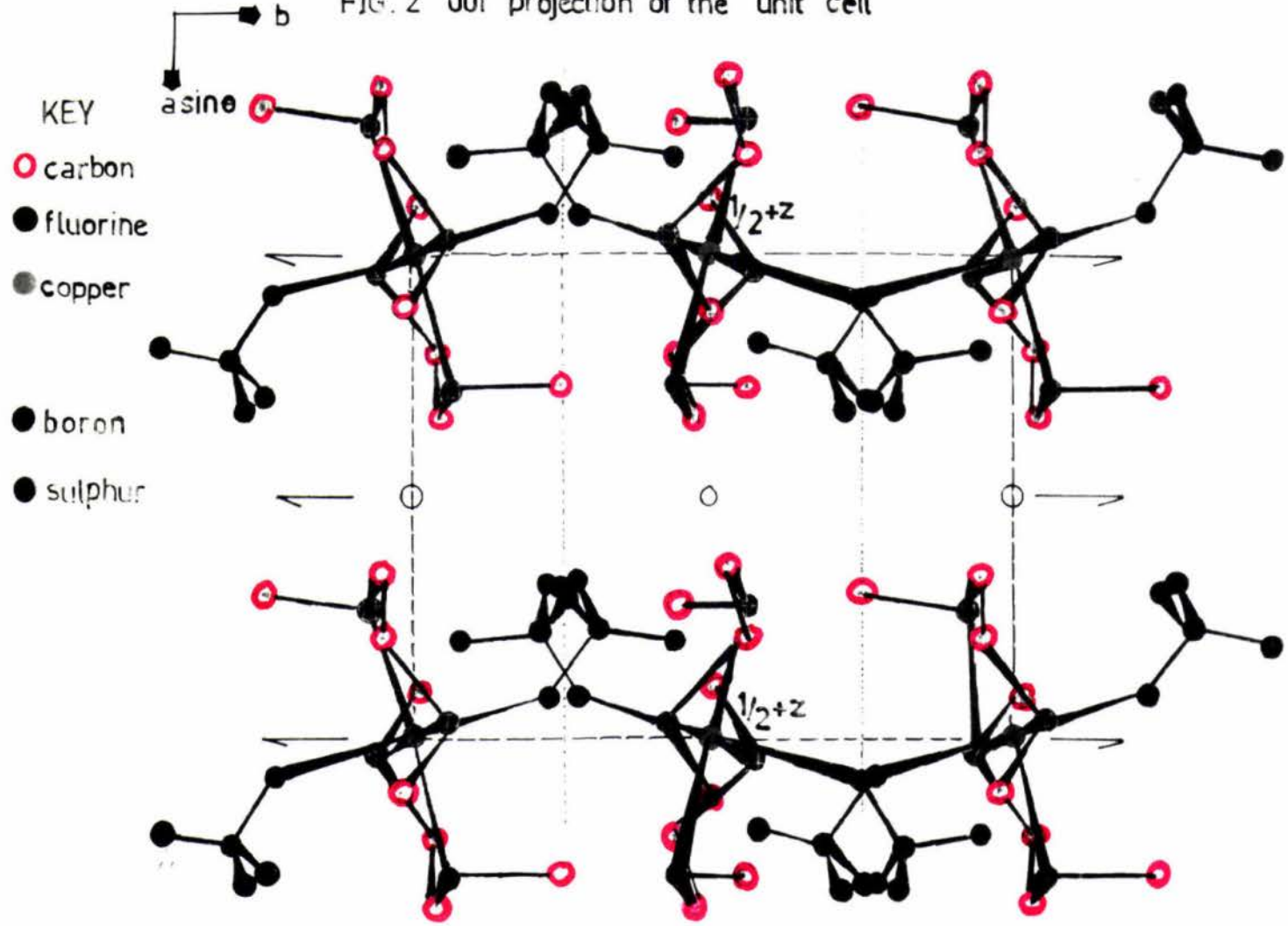

TABLE V - INTERATOMIC DISTANCES (ANGSTRÖMS)

Bonded Distances

Cu(1)-S(2)	2.315±0.002	C(4)-H(20)	1.00
Cu(1)-S(3)	2.319±0.002	C(4)-H(21)	0.88
Cu(1)-F(9)	2.579±0.005	C(4)-H(22)	0.82
S(2)-C(4)	1.783±0.007	C(5)-H(13)	0.92
S(2)-C(6)	1.83 ±0.01	C(5)-H(14)	0.90
S(3)-C(5)	1.800±0.008	C(5)-H(15)	0.98
S(3)-C(7)	1.811±0.008	C(6)-H(18)	1.07
C(6)-C(7)	1.37 ±0.01	C(6)-H(19)	0.99
B(12)-F(10)	1.312±0.009	C(7)-H(16)	1.04
B(12)-F(8)	1.346±0.009	C(7)- (17)	0.91
B(12)-F(9)	1.374±0.009		
B(12)-F(11)	1.38 ±0.01		

Non-Bonded Distances

Intramolecular

S(2)-C(7)	2.694±0.009	$S(2)-S(2)^{II}$	3.34
S(3)-C(6)	2.700±0.009	$S(3)-S(3)^{II}$	4.64
C(4)-C(6)	2.77 ±0.01	$C(4)-F(10)^{II}$	3.40
C(5)-C(7)	2.85 ±0.01	$C(4)-S(3)^{II}$	3.51
S(2)-S(3)	3.215	$C(5)-S(2)^{II}$	3.71
		$C(5)-F(9)^{II}$	3.07

Intermolecular Non Bonded Distances

$C(4)^{I} - F(10)^{IV}$	3.20	$C(4)^{I} - F(8)^{III}$	3.41
$C(4)^{I} - C(5)^{III}$	3.91	$C(6)^{I} - F(8)^{IV}$	3.46
$C(7)^{I} - F(8)^{IV}$	3.61		

N.B. The Roman numerals refer to atoms in the unit cell related by the following symmetry transformations.

I	x, y, z	II	$\bar{x}, \bar{y}, \bar{z}$
III	$\bar{x}, \frac{1}{2} - y, \frac{1}{2} + z$	IV	$x, \frac{1}{2} + y, \frac{1}{2} - z$

All interatomic distances and angles were calculated using the computer programs CORFEE(28) and DANTEP(27).

TABLE VI - INTERATOMIC ANGLES (DEGREES)

S(2) -Cu(1)-S(3)	87.86 ± 0.06	H(22)-C(4)-H(21)	124.8
S(2) -Cu(1)-F(9)	93.2 ± 0.1	H(22)-C(4)-H(20)	88.1
S(3) -Cu(1)-F(9)	91.3 ± 0.1	H(22)-C(4)-S(2)	117.0
C(4) -S(2) -C(6)	100.2 ± 0.4	H(21)-C(4)-H(20)	106.6
C(6) -S(2) -Cu(1)	99.2 ± 0.3	H(21)-C(4)-S(2)	108.4
C(4) -S(2) -Cu(1)	108.7 ± 0.2	H(20)-C(4)-S(2)	107.9
C(5) -S(3) -C(7)	104.1 ± 0.5	H(14)-C(5)-H(13)	103.8
C(5) -S(3) -Cu(1)	106.8 ± 0.3	H(14)-C(5)-H(15)	117.0
C(7) -S(3) -Cu(1)	102.8 ± 0.3	H(14)-C(5)-S(3)	113.2
C(7) -C(6) -S(2)	113.8 ± 0.8	H(13)-C(5)-S(3)	107.6
C(6) -C(7) -S(3)	115.4 ± 0.7	H(13)-C(5)-H(15)	103.8
F(10)-B(12)-F(8)	114.1 ± 0.7	H(15)-C(5)-S(3)	110.3
F(10)-B(12)-F(9)	111.3 ± 0.6	H(19)-C(6)-H(18)	112.6
F(10)-B(12)-F(11)	106.6 ± 0.8	H(19)-C(6)-C(7)	106.1
F(8) -B(12)-F(9)	114.1 ± 0.6	H(19)-C(6)-S(2)	105.1
F(8) -B(12)-F(11)	106.9 ± 0.6	H(18)-C(6)-C(7)	115.9
F(9) -B(12)-F(11)	102.8 ± 0.7	H(18)-C(6)-S(2)	103.0
H(17)-C(7) -H(16)	118.1	H(17)-C(7)-C(6)	102.9
H(17)-C(7) -S(3)	103.5	H(16)-C(7)-C(6)	117.0
H(16)-C(7) -S(3)	115.3		

found in the structure determination of bis(ethylenediamine) copper(II) fluoroborate [Cu(II)$(en)_2(BF_4)_2$](33), where the Cu(II)-N bonds are 2.02 ± 0.01Å and 2.03 ± 0.01Å in length, and the Cu(II)-F bonds are both 2.56 ± 0.01Å long. Predicted values in this case are 2.54Å for the Cu(II)-F bonds as above, and 2.00Å for the Cu(II)-N equatorial bonds assuming covalent radii of 0.70Å for the nitrogen, and 1.3Å for the Cu(II) atom.

The average Cu(II)-S bond length at 2.317Å is thus slightly shorter than expected for a single bond, which may indicate a very slight degree of π bonding or a highly covalent bond (84,85). Cu(II)-S bond lengths which have been found in other complexes with varying stereochemistries are listed in Table VII. On comparison with these, it can be seen that the average copper-culphur distance found in this complex, Cu(II)$(DTH)_2(BF_4)_2$, agrees favourably with that found in three of the complexes listed (34,54,55). However, it is significantly longer than the distances reported for three other structures(35,39,40), and slightly shorter than those found in two of the complexes(36,37). One of the complexes(38) which has a square planar stereochemistry has one type of Cu(II)-S bond which is significantly shorter than that found in Cu(II)$(DTH)_2(BF_4)_2$, while the other is slightly longer.

The S-Cu(II)-S bond angle of 87.86 degrees is slightly smaller than the expected value of 90 degrees. This decrease is probably due to the chelate effect since it is very similar to the value found for the N-Cu(II)-N angle in Cu(II)$(en)_2(BF_4)_2$(33), [86.4 ± 0.5 degrees]. The Cu(II)-F distance is very similar to that found in Cu(II)$(en)_2(BF_4)_2$, although it is slightly longer than expected [2.58Å cf. 2.54Å]. At such a distance [2.58Å compared to a theoretical single covalent bond distance of 2.02Å for an undistorted environment] the fluorine atom can be said to be "semi-co-ordinated" to the copper, where this term implies weak bonding at a definite distance(32,33).

The average C-S bond length is 1.806 ± 0.011Å, which is very similar to the expected single covalent distance of 1.81Å. Similar values were obtained by Larsen in the structure determination of (tetracarbonyl-dithiaoctane)chromium(o) (47), where the average C-S distance was found to be

TABLE VII - COMPARISON OF Cu(II)-S BONDLENGTHS OF $Cu(II)(DTH)_2(BF_4)_2$ WITH THOSE OF OTHER STRUCTURES

COMPOUND	FORMULA	STEREO-CHEMISTRY	Cu(II)-S DISTANCE(Å)	Ref.
bis(thiosomicarbazide)copper(II)nitrate	$Cu(NH_2NHC(NH_2)S)_2(NO_3)_2$	tetragonal	2.286	(39)
bis(thiosemicarbazide)copper(II)sulphate	$Cu(NH_2NHC(NH_2)S)_2SO_4$	square pyramidal	2.259,2.266	(40)
bis(N,N-di-ethyldithiocarbamato) copper(II)	$Cu(CS_2.NEt_2)_2$	square pyramidal	2.32	(54)
bis(N,N-di-n-propyldithiocarbamato) copper(II)	$Cu(CS_2.NPr^n{}_2)_2$	tetragonal pyramidal	2.325	(55), (41)
bis(N-cyclohexylthiopicolinamidato) copper(II)	$C_{24}H_{30}CuN_4S_2$	square planar	2.252,	(35)
bis(pyrolidonecarbodithioato)copper(II)	$Cu(CS_2.NC_4H_8)_2$	sq. planar	2.342,2.345	(37)
bis(N-methyl-N-phenyldithiocarbamato) copper(II)	$Cu(CS_2.NMePh)_2$	sq. planar	2.33, 2.27	(38)
dichlorobis(tetramethylthiourea) copper(II)	$Cu(SCN_2Me_4)_2Cl_2$	distorted sq. planar	2.306,2.323	(34)
NN'tetramethylene bis-(2 pyridinaldimine) thiourea copper(II) perchlorate	$Cu(C_{16}H_{18}N_4)(SC(NH_2)_2)_2(ClO_4)_2$	trigonal bipyramidal	2.344	(36)
bis-(2,2'bipyridyl)thiourea copper(II) perchlorate	$Cu(C_{10}H_8N_2)_2(SC(NH_2)_2)(ClO_4)_2$	trigonal bipyramidal	2.344	(36)
bis(2,5-dithiahexanetetrafluoroborate) copper(II)	$Cu(CH_3SCH_2CH_2SCH_3)_2(BF_4)_2$	distorted octahedral	2.317	(This work)

1.817 ± 0.001Å. However, values as high as 1.86Å have been reported for C-S single bonds(52). All the Cu(II)-S-C and C-S-C bond angles are approximately tetrahedral, suggesting that the sulphur atoms are probably sp^3 hybrids.

As previously mentioned, the C-C bond was found to be unusually short at 1.37 ± 0.01Å. In comparison with other C-C bonds, its length lies between that given for a double bond [1.35Å] and that of a single bond [1.54Å] and is comparable to a delocalized carbon-carbon bond, as in benzene [1.37 - 1.42Å, (43,38,36)]. As spectroscopic, chemical analysis(21) and mass spectrometry had shown the ligand bound to the copper to be dithiahexane, with a C-C single bond, it was thought that the thermal motion of the two atoms involved in the bond may be responsible for an apparent shortening of the bond. This is because the atomic co-ordinates resulting from a crystal structure analysis, represent maxima in the electron density arising from the combined effects of the atomic structure and thermal displacement. When the distance between atoms is computed, it is the distance between a pair of these positions, and as such, is only valid when the thermal displacements are negligibly small. Cruickshank showed that an immediate consequence of anisotropic vibrations, is that the maxima of atomic peaks in electron density maps are closer to the centre of rotation than they would be otherwise, resulting in an apparently decreased bond length(45,46). Busing and Levy(51) have shown that useful estimates of corrections needed for thermal effects can be made from simplified models of the vibrating system of a pair of atoms.

Where w_1 and w_2 are the R.M.S. amplitudes of vibration of atoms 1 and 2, perpendicular to the bond between them, the corrected bond length R_1 is related to the uncorrected value R_0 by the expression

$$R_1 = R_0 + w^2/2R_0$$

The value of w^2 varies depending on the model assumed. These models are as follows:

(a) If the two atoms are vibrating as a whole in phase, then w^2 is a minimum, i.e.

$$w^2_{min} = (w_1 - w_2)^2$$

(b) If it is assumed that the two atoms are vibrating as a whole, but atom(2) is executing an independent motion superimposed on this, then the "riding" model applies

$$w^2_{riding} = w_2^2 - w_1^2$$

(c) If the two atoms are vibrating independently, e.g. intermolecular distances

$$w^2_{ind} = w_1^2 + w_2^2$$

(d) If the two atoms are vibrating completely out of phase, then w^2 is a maximum

$$w^2_{max} = (w_1 + w_2)^2 .$$

The computer program CORFEE(28) was used to calculate the atomic distribution in terms of the principal axis displacements, and the angle these made with the -C-C- bond. If μ_i^2 represents the mean square displacement parallel to the principal axis i of the distribution, and γ_i is the direction cosine of R_0 with respect to this axis then

$$\bar{w}^2 = \sum_{i=1}^{3} (1 - \gamma_i^2)\mu_i^2$$

Table VIII gives the R.M.S. components of thermal displacement along the principal axis R in angströms, together with the angle between R and the vector between atoms 6 and 7.

TABLE VIII

Atom	R	R.M.S. values (Å)(μi)	Angle (Degrees)
C6	1	0.18 ± 0.01	78 ± 4
	2	0.27 ± 0.01	12 ± 4
	3	0.49 ± 0.01	85 ± 2
C7	1	0.22 ± 0.01	81 ± 11
	2	0.26 ± 0.01	26 ± 4
	3	0.42 ± 0.01	64 ± 3

From these values $\bar{w}_6^2$ was calculated as 0.2712, and $\bar{w}_7^2$ as 0.206. The following results were obtained for the corrections

$$R_0 = 1.3719\text{Å}$$
$$\text{Lower Bound} = 1.3735\text{Å}$$
$$\text{Upper Bound} = 1.7182\text{Å}$$

The "riding" model cannot be applied, as to apply such a

correction, the mean square displacement of atom B in any direction should never be less than the corresponding displacement for atom A. This is not the case for C(6) and C(7). As the upper bound value is too large (where w^2 is maximum), and the lower bound value is not much different from the uncorrected value (where w^2 is minimum), it would appear that none of the models described for the vibrating systems of the two atoms are satisfactory. However, as the expected bond length lies between the upper and lower bound values, it is possible that the thermal motion of the atoms is more complex than the above models allow, and as such, could still be responsible for the short bond.

The bond lengths resulting from the refined disorder model are shown in Table IX, where the numbering system is the same as that in Figure 3. In this model C-C bond distances of approximately 1.5Å would be expected between C_{VI} and C_{VIII}, and C_{VII} and C_{IX}. However, such bond distances were not obtained, those which were being difficult to interpret. It was thus decided that this particular disorder model was ineffective, and it was rejected.

TABLE IX - BOND LENGTHS OBTAINED FROM THE REFINED DISORDER MODEL

Bond	Length	Bond	Length
C_{VI}-C_{VII}	0.74Å	C_{VIII}-C_{IX}	0.57Å
C_{VI}-C_{VIII}	1.38Å	C_{VII}-C_{VIII}	1.25Å
C_{VI}-C_{IX}	1.45Å	C_{VII}-C_{IX}	1.60Å
C_{VI}-S_2	1.66Å	C_{VIII}-S_3	1.87Å
C_{VII}-S_2	1.92Å	C_{IX}-S_3	1.81Å

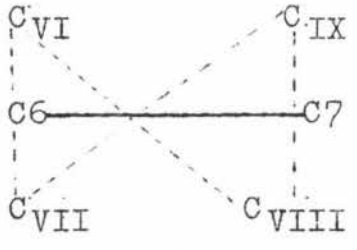

Figure 3. Diagram of the Disorder Model Proposed for the Bridging Carbon Atoms in $Cu(II)(DTH)_2(BF_4)_2$

A similarly short C-C bond has been reported by Cotton and Weaver(53) in the X-ray structure determination of

$Co(DTH)_2(ClO_4)_2$, where the bond length between the two bridging carbons of the DTH ligand, although of low accuracy is 1.30 ± 0.05Å. Shortened C-C bonds have also been observed in Cu-S-C-C-N rings chelated to Cu(I) in the structure determination of cyclo-di-μ { bis[2-(N,N-dimethylamino)ethyl] disulphide } dicopper(I) tetrafluoroborate(57) [1.46(4), 1.47(4), 1.48(3)Å] However, reports of structures of other Cu(II) complexes with similar ligand systems show C-C bonds approximately 1.5Å in length (33,47), and structure determinations of some cyclic thioethers with -S-C-C-S- sequences and no metal ions show similar C-C bond lengths of 1.49 - 1.50Å (56).

Because the copper atom is situated on a centre of symmetry, the copper and the four sulphur atoms must be co-planar, the equation of this plane being,

$$-0.278x + 0.9131y - 0.29672 = 0$$

Here x, y and z are orthoganol co-ordinates in Angströms related to the crystallographic axis by

$$x = ax + cz \cos\beta,$$
$$y = by$$
$$z = cz \sin\beta.$$

The distances of the two ring carbons C(6) and C(7) from this plane were calculated to be -0.71Å and -0.12Å, so that both are on the same side of the plane. Such a conformation of the five membered ring is unexpected as the usual arrangement is a gauche configuration as seen in $Cu(II)(en)_2(BF_4)_2$. In the latter structure, one of the carbon atoms is 0.4Å above the plane containing the copper and two nitrogen atoms, while the other is 0.32Å below it(33). Thus the shortening of the C-C bond is probably due to some sort of disorder which is random in this part of the molecule, and as such cannot be satisfactorily accounted for by a simple model.

The C-C-S bond angles within the rings were approximately tetrahedral, although larger than the corresponding C-C-N angles found in $Cu(II)(en)_2(BF_4)_2$(33). However, they are very similar to those found in $Cu(II)(DTO)_2BF_4$ (see Chapter IV), and in some other five membered rings(57,58). The methyl carbons displayed approximate tetrahedral stereochemistry, with normal C-H bond distances (see Tables V and VI). Deviations from tetrahedral angles are often associated with terminal methyl groups, and are not unusual(72).

The BF_4^- ion was weakly co-ordinated to the Cu(II) atom through F(9), and the fluorine atoms were approximately tetrahedrally bound to the boron atom at varying distances [1.312 ± 0.009Å, 1.346 ± 0.009Å, 1.374 ± 0.009Å, 1.38 ± 0.01Å] all of which are considerably shorter than the expected distance of 1.52Å. Values given for the B-F bond length in a free BF_4^- ion are 1.43Å and in a BF_3 group 1.30Å(43). This decrease in bond length is attributed to increased π overlap between the empty 2p orbitals of the boron, and the full 2p orbitals of the fluorine, or, to the ionic character of the bond which may result because of the electronegativity difference between B and F(44). Although the bond lengths obtained from the structure determination are shorter than expected, they are similar to those found in the ethylene diamine structure(33) [1.41 ± 0.03, 1.37 ± 0.02, 1.30 ± 0.03, 1.38 ± 0.03Å]. However, there are numerous approaches between the fluorine atoms, and the carbon and sulphur atoms of other molecules, the shortest of these being 3.20Å (see Table V). It may be, that the combined effects of these contacts, and the semi-co-ordinate bond between one of the fluorines and the Cu(II) ion, result in these variations of bond length.

CHAPTER IV

STRUCTURE DETERMINATION OF $Cu(I)(DTO)_2BF_4$

1. Data Collection

As for the previous structure, intensity measurements were made on a Hilger and Watts four circle diffractometer controlled by a P.D.P./8I computer, using MoKα radiation. The crystal was mounted along its needle axis, [c], and the 2θ, ω, Ø and settings were determined as before. The cell parameters obtained by use of these values for 12 reflections in a least squares refinement of the orientation matrix were:

a = 14.581(2)Å
b = 13.421(2)Å
c = 10.781(2)Å
α = β = γ = 90.0 degrees.

Intensities were measured as before with a 2θ-ω scan through each reflection, which this time consisted of 35 steps of 0.02 degrees, each lasting 1.6 seconds. Background counts were taken for 7 seconds each side of the scan, and, as a check on alignment, crystal damage, etc., three standard reflections, viz. 080, 730, and 225 were measured after every 75 readings. The data was measured in two shells, θ = 0-20 degrees and θ = 20-27 degrees. The total number of intensity measurements within the first shell was 2318, and in the second shell was 3432, the equivalent reflections measured being hkl and $\bar{h}kl$.

2. Data Reduction

Integrated intensities were calculated as before using the computer program HILGOUT(81), and the data were corrected for Lorentz and polarization effects in the usual way(23). Except for systematic absences, all data were retained, none being rejected as not significantly above background. The maximum variation in the intensities of the standard reflections of the whole data collection was less than 3%, and no decay corrections were therefore applied. For MoKα radiation, the linear absorption coefficient, μ is 14.65 cm^{-1}. As the crystal used had approximate dimensions of 0.6 x 0.4 x 0.4mm, the cylindrical absorption coefficients over the range of sin θ values in the data collection varied from 2.69 to 2.63. Therefore, absorption corrections were

considered unnecessary. Of the 2051 reflections resulting from the first shell of data, 309 had intensities less than σ, 184 between σ and 2σ, 199 between 2σ and 3σ, and 1359 greater than 3σ. For the 20-27 degree shell, the resulting 2378 reflections contained 1196 with intensities less than σ, 600 between σ and 2σ, 251 between 2σ and 3σ, and 331 greater than 3σ. It had already been noted that the Weissenberg photographs showed a marked decrease in intensity for reflections of high 2θ values, suggesting that there was some disorder in the crystal acting to increase the thermal vibration of the atoms. The equivalent reflections were then averaged to give 1024 reflections in the first shell of data, and 1189 in the second shell.

3. Structure Determination

(a) Patterson synthesis:

Patterson recognized that the squares of structure factors were independent of their associated phase angles, and that a Fourier summation using these could always be computed(59), using the following expression

$$P_{uvw} = \frac{1}{v^2} \sum_{-h}^{h} \sum_{-k}^{k} \sum_{-l}^{l} |F_{hkl}|^2 \cos 2\pi (hu + kv + lw).$$

Thus, whenever u, v, w corresponds to an interatomic vector, a peak will appear in the Patterson map. If there are N atoms present in the unit cell, there will be N^2 peaks in the Patterson map, N of which will occur at the origin. A three dimensional Patterson map was calculated using the reflections of the inner (0-20 deg.) shell of data(25). The space group $Pna2_1$ has equivalent positions

I) x, y, z

II) $\bar{x}, \bar{y}, \frac{1}{2} + z$

III) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$

IV) $\frac{1}{2} + x, \frac{1}{2} - y, z$.

which give rise to heavy atom vectors of the type

$$\pm 2x, \pm 2y, \tfrac{1}{2}; \quad \tfrac{1}{2}, \tfrac{1}{2} \pm 2y, 0; \quad \tfrac{1}{2} \pm 2x, \tfrac{1}{2}, \tfrac{1}{2}$$

The highest peaks in the Patterson map are listed in Table X. Peaks 1, 2 and 3 make a consistent set of heavy atom - heavy atom vectors, and although peaks 4, 5 and 6 were higher than peak 3, they could not be successfully

assigned to the heavy atom vector types expected. The height of peak 3 was much lower than those of peaks 1 and 2, but this was expected because the predicted weighing of the peaks indicated that peaks 1 and 2 should be approximately twice as big as peak 3.

TABLE X - THE MAIN FEATURES OF THE PATTERSON MAP

Peak Number	Peak Size (ρ)	Peak Position	Assigned
1	246	0.077, 0.5, 0.5	$\frac{1}{2}-2x, \frac{1}{2}, \frac{1}{2}$
2	260	0.5, 0.458, 0.0	$\frac{1}{2}, \frac{1}{2}-2y, 0$
3	78	0.423, 0.042, 0.5	$2x, 2y, \frac{1}{2}$
4	120	0.5, 0.271, 0	
5	123	0.25, 0.5, 0.5	
6	84	0.5, 0.375, 0.192	

(b) Fourier synthesis:

The vectors found in the Patterson map gave the x and y co-ordinates of the heavy atom, but left the z co-ordinate unspecified. Hence the z co-ordinate was assigned an arbitrary value of 0.25. The first Fourier calculation(25) phased by the copper atom (as in the first structure), showed numerous peaks, but interpretation was complicated by false symmetry about a mirror plane at z = 0.25. This false symmetry was broken by the inclusion of a second atom, identified as a sulphur atom from its distance from the copper atom and the height of the peak, in the phase calculation. From the resulting electron density map the positions of the remaining three sulphur atoms, a carbon atom, and a fluorine atom were determined. A further map, calculated using the phases of all atoms found, showed peaks representing another carbon and fluorine atom. The remaining atoms, apart from the boron, were identified from two further electron density maps calculated in the same way, and taking into account the expected stereochemistry of the ligand, as for the first structure. A difference Fourier synthesis was required to determine the exact position of the boron atom. At this stage of the structure determination the R factor was 0.277, and a final difference Fourier showed no

large peaks that were not accounted for.

4 Refinement of the Structure

For the initial refinement only the inner shell of data was used, and reflections for which $|F_o|^2 < 2\sigma|F_o|^2$ were omitted to give a total of 868 reflections. Two cycles of full matrix least squares refinement with isotropic thermal parameters reduced R to 0.105, and the weighted R factor to 0.117. The anisotropic refinement of the copper, sulphur and carbon atoms was attempted in blocks, the parameters of the first 11 atoms, and the remaining atoms, being varied in alternate cycles. However, 2 cycles (4 blocks) of anisotropic refinement of the non BF_4^- atoms only reduced the R factor to 0.097 i.e. producing very little improvement.

When an anisotropic refinement of the atoms in the BF_4^- ion was attempted, a degree of disorder became evident. This was not unexpected, since it had already been noted that the isotropic temperature factors of the atoms concerned were higher than expected. A difference Fourier map was calculated to check the positional parameters of the group. In this map, overlapping peaks were observed whose maxima were only slightly shifted from the values given by refinement for all but F(48) which showed a marked shift (numbering of atoms is shown in Figure 7). Using these new parameters, two refinements of the positional and isotropic thermal parameters of the BF_4^- atoms (the parameters of the other atoms in the molecule not being varied), reduced the R factor from 0.114 to 0.082, the weighted R factor dropping from 0.128 to 0.076.

At this stage, because of the small number of observations being used in the calculations, it was decided to include reflections for which $|F_o|^2 > 0\,|F_o|^2$, raising the number to 968. Two further cycles (4 blocks) of least squares refinement using anisotropic temperature factors for all non BF_4^- atoms, and isotropic temperature factors for the BF_4^- atoms, reduced R from 0.091, to 0.077, and the weighted R factor from 0.084 to 0.064. However, the position of the boron atom as determined by the refinement process, with respect to the fluorine atoms, was not in accord with any known stereochemistry for a free BF_4^- group. A difference Fourier, calculated with all the atoms in the

structure as it stood contributing to F_c, showed a peak near the centre of the tetrahedron of fluorine atoms where the boron atom was expected. When the boron was shifted to this position in a refinement cycle, however, the R factor rose. Successive refinements showed that although the R factor initially fell, it did not converge, but in fact began to rise again due to shifts in the parameters of the boron atom. It was also noted that the isotropic temperature factor of the boron was very high at about 40 $Å^2$, and those of the fluorine atoms were also higher than expected at approximately 20$Å^2$, indicating some sort of disorder(60). When the boron atom was placed in this stereochemically reasonable position, and a difference Fourier calculated, a region of high electron density could be seen directly above its position along the y direction. It was thought that this was due to disorder in the BF_4^- group and could be responsible for the shifts observed on refinement.

It was decided that before introducing a disorder model for the BF_4^- group, the data from the 20-27 degree shell should be added, and the refinement repeated. This is because when the number of reflections used in a structure calculation is reduced by omitting all those with $(\sin\theta)/\lambda$ values greater than some specified value, the effect is to spread the atoms and ultimately cause them to overlap. Thus, although stronger reflections of low $(\sin\theta)/\lambda$ values are less affected by small errors in the parameters of trial structures, abnormally high temperature factors can result(23). The addition of the higher angle data, with the restriction that only reflections with $|F_o|^2 > 2\sigma|F_o|^2$ were used in least squares calculations, raised the number of observations to 1177. After two cycles of refinement of the positional and isotropic thermal parameters of all non BF_4^- atoms, the R factor was reduced from 0.148 to 0.109. Two further cycles of least squares refinement in which atoms heavier than carbon, together with the BF_4^- group were allowed anisotropic temperature factors, gave a reliability factor R of 0.102, and a weighted R factor of 0.076, both of which were higher than values obtained with the low angle data (0.077 and 0.064). However, as before

there was no true convergence owing to the disorder in the BF_4^- group.

The BF_4^- group was then refined using a disorder model in which the BF_4 anion was represented as occupying two different positions in the unit cell, each related by a mirror plane through three of the fluorine atoms. This meant that three of the fluorine atoms were shared by the two orientations, the positional parameters of one fluorine (the peak above the boron as seen in the difference Fourier) and the boron atom, being different in each. The populations of the two orientations were estimated from this density map as being approximately 0.8 and 0.2. Such a model proved to be unsatisfactory as the R factor increased on refinement, and the temperature factors of the atoms involved still remained high.

As no difference Fourier map had been calculated since the addition of the high angle data, one was calculated with the atoms of the BF_4^- group omitted from the structure factor calculation. The resulting density map again showed a region of high electron density containing ill defined peaks where the BF_4^- atoms were expected. A three dimensional section of the map is shown in Figure 4, showing the overlapping of peaks. Such a distribution of electron density explained why the refinement of individual atomic parameters with partial multiplicities failed, since such a refinement is not possible if atoms from different contributions to the disordered structure are in very close proximity(61). It was thus decided that the structure determination could be best continued by placing rigid group restrictions on the atoms in question. A similar problem involving thiophene rings which exhibited three fold disorder was successfully dealt with using group refinement methods in the structure determination of thiophene chromium tricarbonyl(60).

The position and orientation of a rigid group in the unit cell can be described by 6 parameters; 3 positional parameters x, y and z, which define the origin of the group, and three angular parameters ϕ, θ and ρ, which specify the orientation of the group, all with respect to the crystal axes. The origin in crystal co-ordinates, is also the

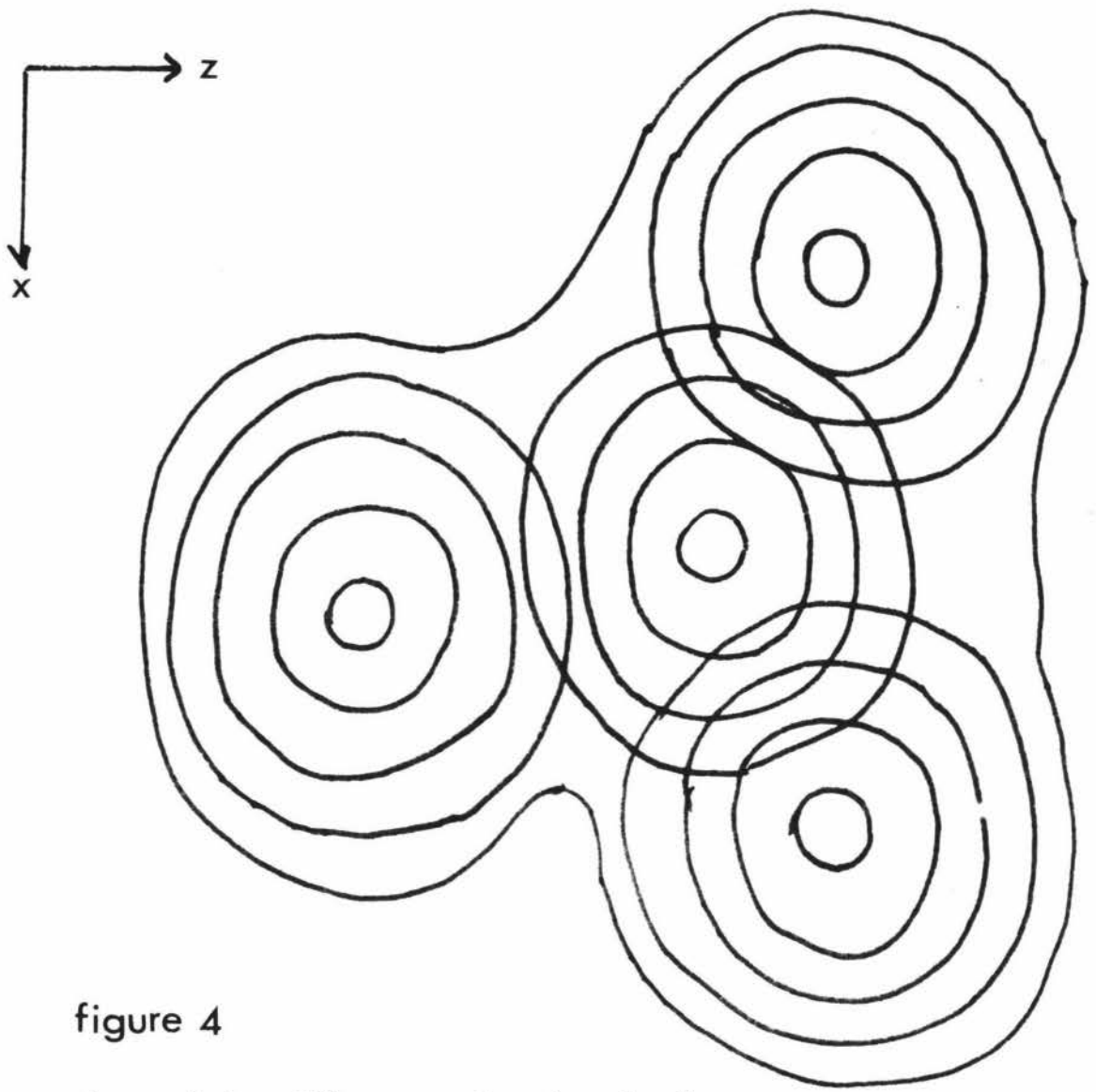

figure 4

section of the difference fourier $f_o - f_c$

with only the CuDTO atoms contributing to f_c $y = 0{\cdot}36$

origin of a cartesian co-ordinate system in which the positions of all the atoms belonging to the group are expressed in Angströms.

The usual stereochemistry of a free BF_4^- ion is a tetrahedron, with BF bond distances of about 1.43Å(43). Calculations of bond distances and angles from the peak maxima of the difference Fourier (e.g. Figure 4), showed that although the geometry of the group was probably tetrahedral, the bond lengths were very varied [1.27, 1.35, 1.26, 1.41Å]. Similar distances have been reported for other structures containing free BF_4^- ions(57,63). It was thus decided to use a B-F distance of 1.34Å, and a F-B-F bond angle of 109.5 degrees to define the tetrahedron. The choice of base point in an isotropic rigid group refinement is arbitrary, but in this case the obvious choice was the boron atom. The co-ordinates in Angströms for each group relative to its own orthonormal axes were thus calculated to be

F	1.34Å	0.0Å	0.0Å
F	-0.447Å	0.0Å	1.263Å
F	-0.447Å	-1.093Å	-0.633Å
F	-0.447Å	1.093Å	-0.633Å
B	0.0Å	0.0Å	0.0Å

The difference Fourier indicated that the disorder in the BF_4^- anion could be two-fold about a C_4 axis of a tetrahedron centred at the boron atom. A model for such disorder is shown in Figure 5. The orientation angles for both groups in this model then had to be determined for use in group refinement. This was done using the fractional co-ordinates of 4 points, v_1, v_2, v_3, v_4 referred to the crystal axes to specify the directions of the group axes xg, yg and zg, as follows(30)

(1) xg was parallel to $(v_2 \leftarrow v_1)$, where $\overleftarrow{v_2v_1}$ was the vector between the boron and a fluorine of the appropriate group.

(2) zg was parallel to xg cross $(v_4 \leftarrow v_3)$ where $\overleftarrow{v_4v_3}$ was a vector calculated to be perpendicular to the vector $\overleftarrow{v_2v_1}$(80), and $v_3 \equiv v_1$.

(3) yg is parallel to zg cross xg as the system used was right handed.

The initial angular and basic co-ordinates calculated for each group were

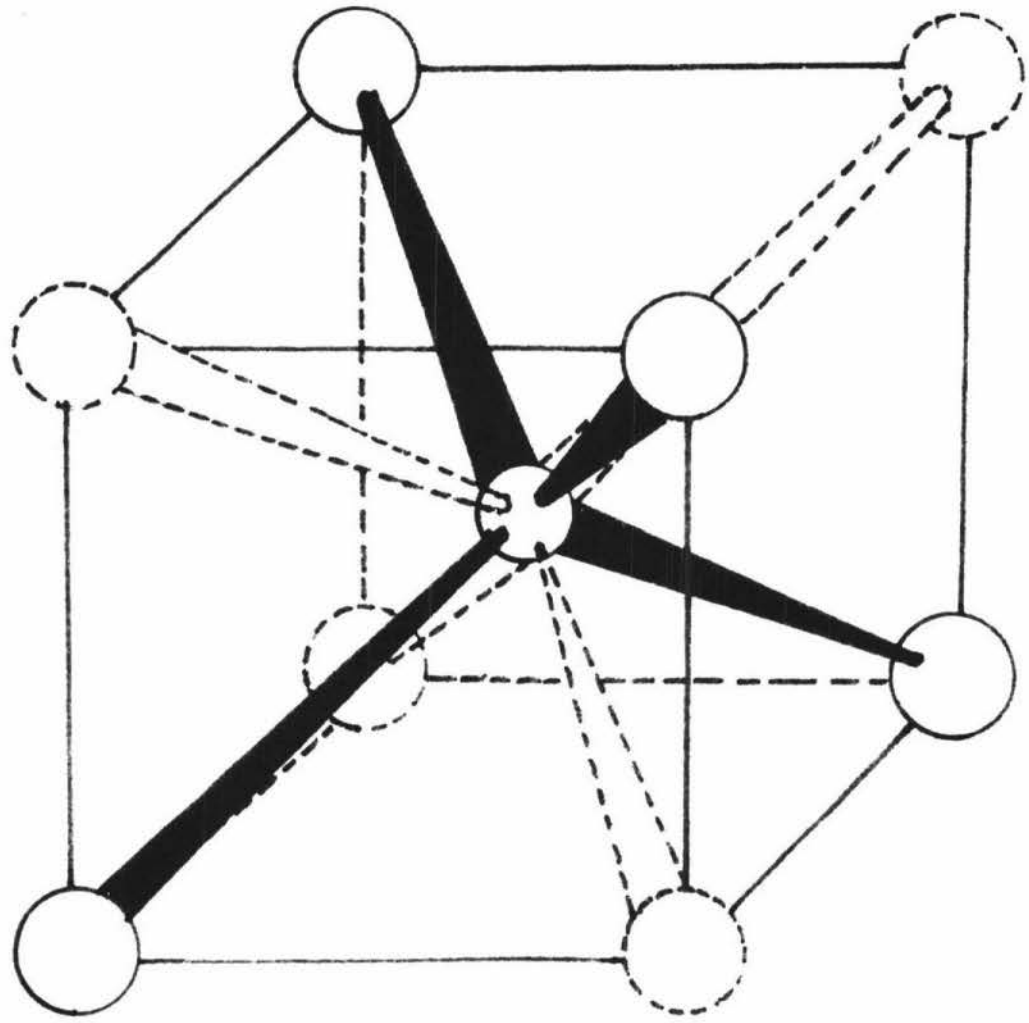

FIG. 5

The disorder model proposed for the BF_4 atoms

	X_{GO}	Y_{GO}	Z_{GO}	ϕ	θ	ρ
Group 1	0.382	0.357	0.173	-127.821	179.110	-82.312
Group 2	0.374	0.353	0.170	175.830	-177.104	-89.383

The model was first refined with one group, each of the atoms having full multiplicity. Three cycles of refinement in which the group parameters only were varied reduced the R factor from 0.129 to 0.107. The second group was then introduced, the atoms being given multiplicities of 0.3, which were complemented by those of the original group at 0.7, giving a reliability factor of 0.105. Limitations of the program used(26) meant that the group atoms could not be refined anisotropically, that the multiplicities of the group atoms could not be varied as a function of the refinement, and that the group temperature parameters could not be varied simultaneously with the individual thermal parameters of the atoms. Thus 8 cycles of refinement were required to find the best combination of the above parameters to obtain the best agreement between the observed and calculated structure factors. The R factor finally converged with R at 0.089, the weighted R factor at 0.074 and the standard error in an observation of unit weight, E, at 2.5542 electrons.

The R factor, however, was higher than the lowest value reached using a conventional refinement and the low angle data (0.077) but the reduction of parameters effected by using group refinement methods necessarily causes a worse fit between the observed and calculated structure factors, resulting in an increased R factor. This is because the shift of group parameters is the weighted mean of all the single atom parameters which contribute to it. Thus the group will move more steadily in refinement towards the direction which would be taken by the predominant number of atoms(62).

Hydrogen atoms were located from a difference Fourier with the aid of the computer program HFIND (Appendix 3). This program calculates the approximate positions of the hydrogen atoms using vector methods and assuming a C-H bond distance of 1.08Å and tetrahedral stereochemistry for the carbon atoms. The calculated positions were used to find the approximate positions in the Fourier map, the

correct positions being obtained from peak maxima. The hydrogen atoms were not refined, and were given B values approximately 1.2 times those of the carbon atom to which they were attached(64). Inclusion of the 22 hydrogen atom positions and their associated thermal parameters in the structure factor calculation, reduced the R factor to 0.086, and two further cycles of refinement of all non group atoms saw the R factor finally converge at 0.082, with R_2 at 0.064 and the error in an observation of unit weight being 2.2362 electrons.

A final difference Fourier map revealed two peaks at heights of 0.716 and 0.674 e.A^{-3}, and a trough of -1.108 e.A^{-3} in the vicinity of the BF_4^- group. Presumably the model for disorder is not completely satisfactory. All other peaks and troughs in the final difference Fourier were less than 0.5 and -0.64 e.A^{-3} respectively. The results of the rigid body refinement (Table XI) were almost in complete agreement with the assumed model of two-fold disorder, the only difference being a slight displacement of the rotation due to the positions of the two boron atoms which were not concentric. The disorder is shown in Figure 6. Observed and calculated structure factors have been tabulated (Appendix 2), and the final fractional co-ordinates and isotropic temperature factors of all non group and non hydrogen atoms are shown in Table XII. The anisotropic temperature factors and R.M.S. amplitudes of vibration for the copper and sulphur atoms are shown in Table XIII. The fractional co-ordinates and isotropic temperature factors used for all hydrogen atoms are shown in Table XIV. The numbering system for the non hydrogen atoms corresponds to that in Figures 6 and 7, and the hydrogen atoms are numbered sequentially and also identified by the number of the carbon atom to which they are attached.

5. Description of the Structure

The crystal structure consists of discrete monomeric ions, the nearest contact between the anion and cation being 3.25Å (Table XVII). Interatomic distances are shown in Tables XV, XVI, XVII and interatomic angles in XVIII and XIX. The overall geometry of the molecule is shown in Figure 7 and the arrangement of ions in the unit cell is

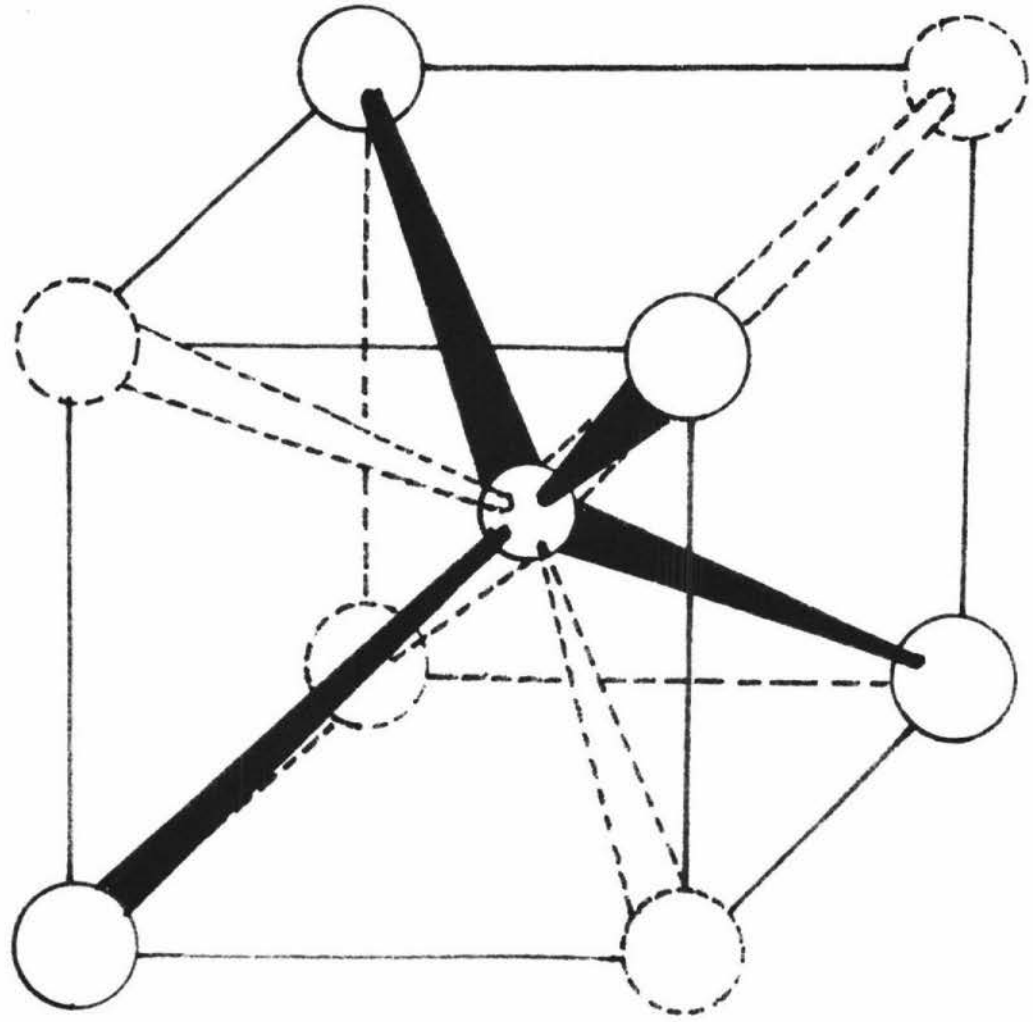

FIG. 5

The disorder model proposed for the BF_4 atoms

TABLE XI

Results of the rigid body refinement

	X_B	Y_B	Z_B	ϕ	θ	ρ	B_{GRP}
Group 1	0.377	0.350	0.176	-151.999	178.897	-85.993	3.796
Group 2	0.397	0.346	0.174	152.196	-175.838	-140.289	4.286

Atomic Parameters

Group 1

AGRP	AIG	BATOM	Xc	Yc	Zc
F	0.75	9.626	0.370	0.349	0.052
F	0.75	11.986	0.455	0.395	0.209
F	0.75	8.938	0.376	0.257	0.219
F	0.75	9.194	0.306	0.401	0.223
B	0.75	13.000	0.377	0.350	0.176

Group 2

F	0.25	9.626	0.458	0.306	0.095
F	0.25	11.986	0.428	0.336	0.290
F	0.25	8.938	0.316	0.300	0.163
F	0.25	9.194	0.386	0.443	0.148
B	0.25	13.000	0.397	0.346	0.174

N.B. AGRP = identification of the atom in the group.
AIG = multiplicity of atom in the group.
BATOM = temperature factor of the atom in the group.
BGRP = temperature factor of group.
B = BATOM + BGRP for each atom.

TABLE XII - FRACTIONAL CO-ORDINATES AND ISOTROPIC[a] TEMPERATURE FACTORS OF ALL NON GROUP AND NON HYDROGEN ATOMS

No.	Atom	x/a	y/b	z/c	B(Å²)
1	Cu	0.2094 (1)	0.0279 (1)	0.2595 (9)	*
2	S	0.3487 (3)	0.0314 (3)	0.355 (1)	*
3	S	0.1527 (3)	-0.1244 (3)	0.198 (1)	*
4	S	0.1332 (3)	0.1174 (3)	0.411 (1)	*
5	S	0.1882 (3)	0.1011 (3)	0.067 (1)	*
6	C	0.321 (1)	0.130 (1)	0.464 (2)	5.7 (4)
7	C	0.137 (1)	-0.094 (1)	0.037 (2)	6.8 (4)
8	C	0.349 (1)	-0.087 (1)	0.446 (2)	7.3 (5)
9	C	0.224 (1)	0.119 (1)	0.522 (2)	6.9 (4)
10	C	0.039 (1)	-0.122 ((1)	0.266 (3)	8.7 (5)
11	C	0.113 (1)	0.006 (1)	0.006 (2)	6.0 (4)
12	C	0.133 (1)	0.243 (1)	0.347 (2)	6.9 (4)
13	C	0.087 (1)	0.318 (1)	0.425 (2)	8.8 (5)
14	C	-0.013 (1)	-0.212 (2)	0.248 (3)	13.6 (7)
15	C	0.300 (1)	0.083 (1)	-0.006 (2)	8.0 (5)
16	C	0.300 (2)	0.108 (2)	-0.147 (3)	12.4 (7)
17	C	0.427 (2)	-0.083 (2)	0.541 (3)	11.9 (7)

a * Anisotropic temperature factors of atoms 1-5 are shown in Table XIII.

All numbers in parentheses are standard deviations in the least significant figure.

Isotropic temperature factors are of the form $\exp[-B(\sin^2\theta)/\lambda^2]$ where $B = 8\pi^2\mu^2$ and μ^2 is the mean square amplitude of vibration.

TABLE XIII - ANISOTROPIC TEMPERATURE FACTORS AND R.M.S. AMPLITUDES OF VIBRATION OF THE Cu AND S ATOMS

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	0.0072(1)	0.0083(1)	0.0113(2)	0.0001(1)	-0.0002(2)	-0.0012(2)
S (2)	0.0053(2)	0.0099(4)	0.0152(6)	0.0003(3)	0.0003(3)	-0.0001(5)
S (3)	0.0071(3)	0.0068(3)	0.0188(8)	0.0002(3)	-0.0001(4)	-0.0010(4)
S (4)	0.0064(2)	0.0076(3)	0.0106(5)	-0.0001(3)	0.0011(3)	-0.0003(4)
S (5)	0.0079(3)	0.0077(4)	0.0116(5)	0.0009(3)	0.0016(3)	-0.0002(4)

Atom	R.M.S.D(1)(Å)	R.M.S.D(2)(Å)	R.M.S.D(3)(Å)
Cu(1)	0.247	0.277	0.286
S (2)	0.238	0.299	0.301
S (3)	0.246	0.277	0.334
S (4)	0.237	0.262	0.275
S (5)	0.242	0.266	0.307

The anisotropic temperature factors are of the form

$$\exp\left[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)\right]$$

Standard deviations in the least significant figure are given in parentheses following each parameter.

R.M.S.D values correspond to the root mean square amplitudes of vibration in Angströms of the atom along the three principal axes of its vibration ellipsoid.

TABLE XIV - FRACTIONAL CO-ORDINATES AND ISOTROPIC TEMPERATURE FACTORS OF THE HYDROGEN ATOMS

No.	Atom	x	y	z	B(Å²)
18	H (6)	0.328	0.197	0.420	6.84
19	H (6)	0.370	0.133	0.532	6.84
20	H (7)	0.091	-0.142	-0.005	8.16
21	H (7)	0.188	-0.118	-0.018	8.16
22	H (8)	0.358	-0.140	0.390	8.76
23	H (8)	0.289	-0.075	0.485	8.76
24	H (9)	0.224	0.060	0.585	8.28
25	H (9)	0.209	0.175	0.580	8.28
26	H(10)	-0.002	-0.064	0.234	10.44
27	H(10)	0.037	-0.110	0.357	10.44
28	H(11)	0.046	0.015	0.032	7.20
29	H(11)	0.112	0.010	-0.061	7.20
30	H(12)	0.105	0.243	0.256	8.28
31	H(12)	0.197	0.265	0.319	8.28
32	H(13)	0.020	0.300	0.440	10.56
33	H(13)	0.095	0.312	0.512	10.56
34	H(13)	0.110	0.385	0.370	10.56
35	H(14)	0.003	-0.264	0.243	16.32
36	H(14)	-0.002	-0.225	0.158	16.32
37	H(14)	-0.052	-0.194	0.305	16.32
38	H(15)	0.321	0.008	-0.002	9.6
39	H(15)	0.351	0.115	0.031	9.6
40	H(16)	0.258	0.157	-0.139	14.88
41	H(16)	0.247	0.071	-0.171	14.88
42	H(16)	0.342	0.050	-0.180	14.88
43	H(17)	0.466	-0.074	0.476	14.28
44	H(17)	0.403	-0.023	0.596	14.28
45	H(17)	0.429	-0.146	0.568	14.28

Note: the numbers in parentheses refer to the carbon atom to which that particular hydrogen atom is attached.

100 projection of the

$Cu(DTO)_2BF_4$ molecule

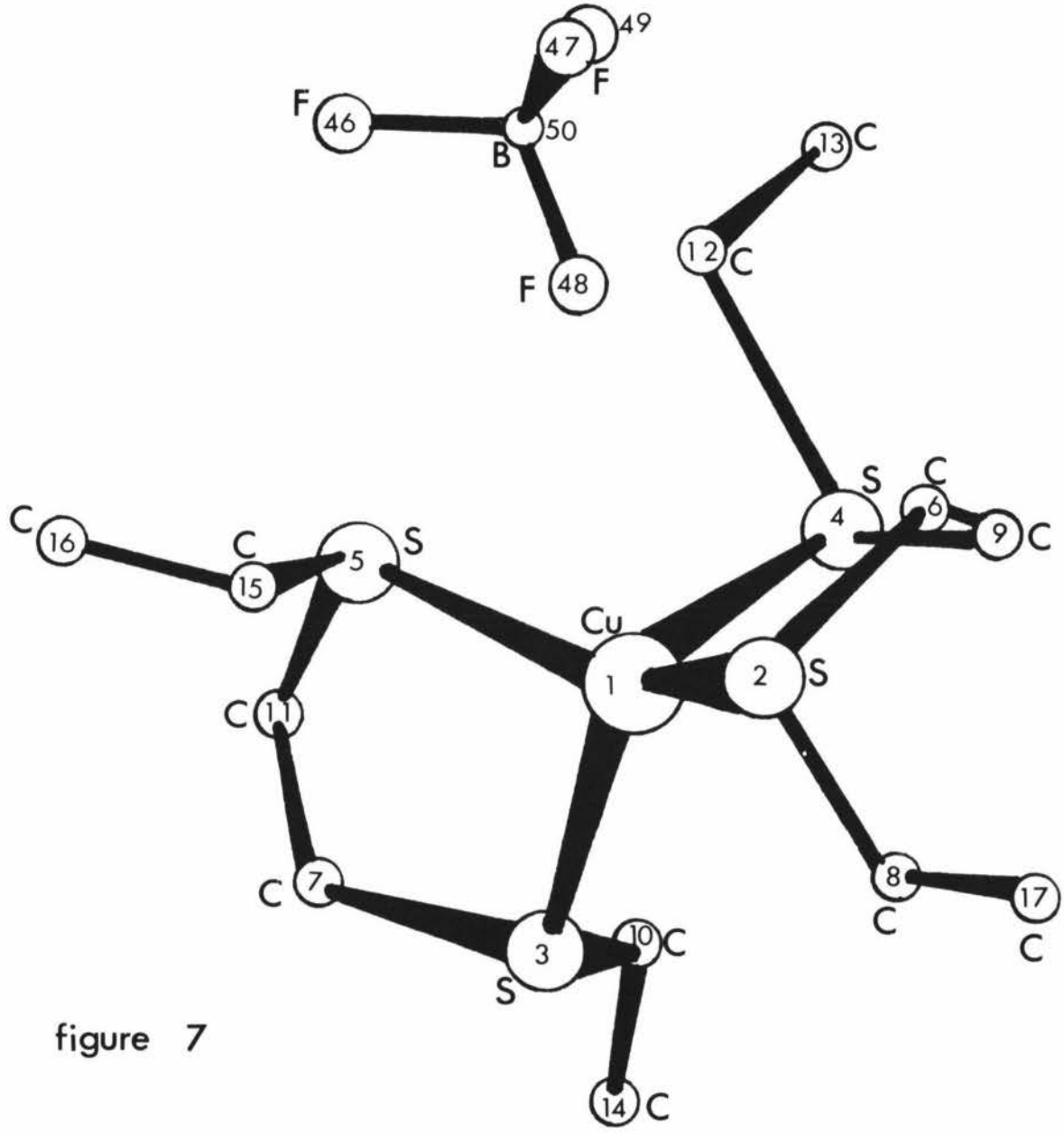

figure 7

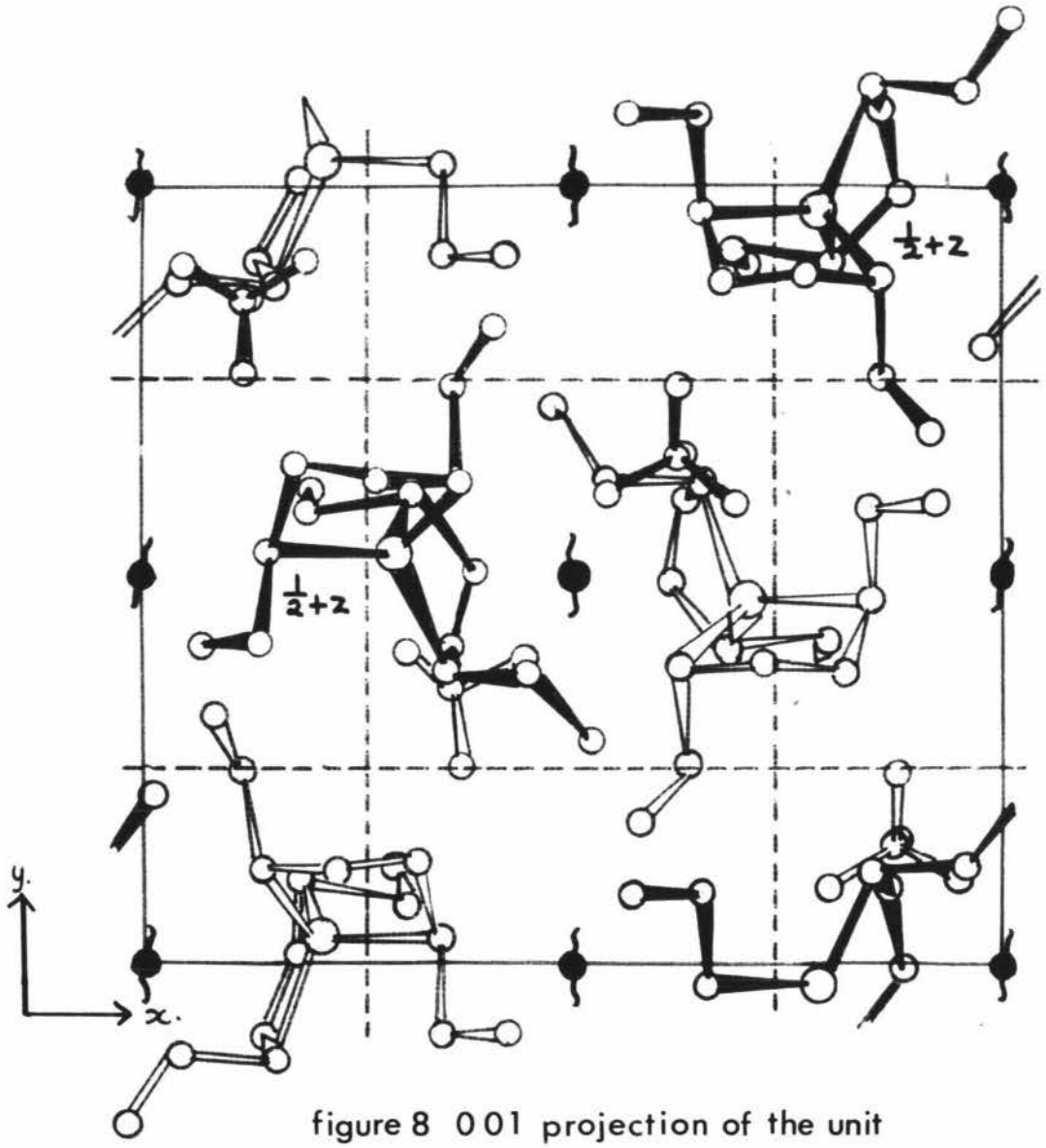

figure 8 0 0 1 projection of the unit cell containing $Cu_1(DTO)_2BF_4$

TABLE XV - INTRAMOLECULAR DISTANCES[a]

Cu(1) - S(2)	2.280 ± 0.004	C(8) - C(17)	1.52 ± 0.03
Cu(1) - S(3)	2.303 ± 0.005	C(10) - C(14)	1.45 ± 0.02
Cu(1) - S(4)	2.310 ± 0.005	C(12) - C(13)	1.47 ± 0.02
Cu(1) - S(5)	2.318 ± 0.005	C(15) - C(16)	1.56 ± 0.03
S(2) - C(6)	1.81 ± 0.02	B(50) - F(46)	1.34
S(2) - C(8)	1.87 ± 0.02	B(50) - F(47)	1.34
S(3) - C(7)	1.80 ± 0.02	B(50) - F(48)	1.34
S(3) - C(10)	1.81 ± 0.02	B(50) - F(49)	1.34
S(4) - C(9)	1.78 ± 0.02	B(55) - F(51)	1.34
S(4) - C(12)	1.81 ± 0.02	B(55) - F(52)	1.34
S(5) - C(11)	1.81 ± 0.02	B(55) - F(53)	1.34
S(5) - C(15)	1.82 ± 0.02	B(55) - F(54)	1.34
C(6) - C(9)	1.55 ± 0.02		
C(7) - C(11)	1.44 ± 0.02		

[a] Interatomic Distances were calculated using the computer program CORFEE(28).

TABLE XVI - INTRAMOLECULAR DISTANCES INVOLVING HYDROGEN ATOMS (Å)[a]

C(6) - H(18)	1.02	C(13) - H(32)	1.00
C(6) - H(19)	0.99	C(13) - H(33)	0.99
C(7) - H(20)	1.01	C(13) - H(34)	1.12
C(7) - H(21)	0.97	C(14) - H(35)	0.76
C(8) - H(22)	0.94	C(14) - H(36)	0.99
C(8) - H(23)	0.98	C(14) - H(37)	0.85
C(9) - H(24)	1.04	C(15) - H(38)	1.02
C(9) - H(25)	1.05	C(15) - H(39)	0.93
C(10) - H(26)	1.03	C(16) - H(40)	0.89
C(10) - H(27)	1.04	C(16) - H(41)	0.91
C(11) - H(28)	1.01	C(16) - H(42)	1.07
C(11) - H(29)	0.75	C(17) - H(43)	0.95
C(12) - H(30)	1.08	C(17) - H(44)	1.05
C(12) - H(31)	0.99	C(17) - H(45)	0.85

[a] Interatomic Distances were calculated using the computer program DANTEP(27).

TABLE XVII - SOME NON BONDED DISTANCES (Å)[a]

INTRAMOLECULAR NON BONDED DISTANCES

S(2)	- S(4)	3.41	S(2)	- F(48)	3.39
S(3)	- S(5)	3.38	S(3)	- F(45)	3.85
S(4)	- S(5)	3.80	S(2)	- S(3)	3.93
C(6)	- F(48)	3.25	C(15)	- F(48)	3.57
C(15)	- F(53)	3.48	C(15)	- F(46)	3.77
C(16)	- F(46)	4.04	F(47)	- H(28)	2.42
B(50)	- B(55)	0.30	F(53)	- H(31)	2.46

INTERMOLECULAR NON BONDED DISTANCES

H(33)I	- H(36)II	2.38	H(34)I	- H(38)III	2.38
H(34)I	- H(42)III	2.39	F(47)I	- H(26)III	2.37
F(54)I	- H(24)IV	2.35	F(52)I	- H(20)IV	2.25
			F(54)I	- H(26)III	2.48
F(47)I	- C(10)III	3.33	F(52)I	- C(7)IV	2.941
F(54)I	- C(9)IV	3.146	F(54)I	- C(10)III	3.501
F(51)I	- H(45)II	2.73			
S(2)I	- H(32)III	3.49	C(7)I	- H(18)IV	3.09
S(4)I	- F(52)III	3.32	C(10)I	- H(29)II	3.28
S(4)I	- H(20)II	3.40	C(11)I	- H(27)II	3.04
C(6)I	- H(32)III	3.03	C(15)I	- H(34)IV	3.19
C(16)I	- H(34)IV	3.28	C(17)I	- H(39)II	3.25
F(46)I	- H(27)IV	2.56	C(17)I	- H(30)IV	3.27
F(49)I	- H(24)IV	2.64			

N.B. The Roman Numerals refer to positions related by the following transformations:

I x, y, z II $\bar{x}, \bar{y}, \frac{1}{2} + z$

III $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + 2$ IV $\frac{1}{2} + x, \frac{1}{2} - y, z$

[a] Distances were calculated using the computer program DANTEP(27).

TABLE XVIII - INTERATOMIC ANGLES (DEGREES)

S(2) -Cu(1) -S(3)	117.9±0.2	C(9) -C(6) -S(2)	113.5±1.1
S(2) -Cu(1) -S(4)	95.6±0.2	C(11)-C(7) -S(3)	118.1±1.3
S(2) -Cu(1) -S(5)	121.1±0.2	C(17)-C(8) -S(2)	109.0±1.4
S(3) -Cu(1) -S(4)	119.5±0.2	C(6) -C(9) -S(4)	114.0±1.2
S(3) -Cu(1) -S(5)	94.0±0.2	C(14)-C(10)-S(3)	114.4±1.6
S(4) -Cu(1) -S(5)	110.4±0.2	C(7) -C(11)-S(5)	115.2±1.2
C(6) -S(2) -C(8)	106.5±0.7	C(13)-C(12)-S(4)	115.4±1.4
C(6) -S(2) -Cu(1)	96.1±0.5	C(16)-C(15)-S(5)	113.4±1.5
C(7) -S(3) -C(10)	105.7±0.9	F(48)-B(50)-F(47)	109.6
C(7) -S(3) -Cu(1)	97.1±0.6	F(48)-B(50)-F(46)	109.4
C(9) -S(4) -C(12)	104.2±0.8	F(48)-B(50)-F(49)	109.8
C(9) -S(4) -Cu(1)	97.0±0.6	F(47)-B(50)-F(46)	109.5
C(11)-S(5) -C(15)	106.9±0.8	F(47)-B(50)-F(49)	109.5
C(11)-S(5) -Cu(1)	93.3±0.5	F(46)-B(50)-F(49)	109.0
Cu(1)-S(2) -C(8)	103.0±0.6	F(52)-B(55)-F(53)	109.6
Cu(1)-S(3) -C(10)	101.1±0.6	F(52)-B(55)-F(54)	109.5
Cu(1)-S(4) -C(12)	102.6±0.6	F(52)-B(55)-F(51)	109.2
Cu(1)-S(5) -C(15)	102.1±0.6	F(53)-B(55)-F(54)	108.9
F(53)-B(55) -F(51)	110.1	F(54)-B(55)-F(51)	109.5

TABLE XIX - INTERATOMIC ANGLES INVOLVING HYDROGEN ATOMS (DEGREES)

H(19)-C(6) -H(18)	105.7	H(19)-C(6) -C(9)	112.2
H(19)-C(6) -S(2)	111.0	H(18)-C(6) -C(9)	110.0
H(18)-C(6) -S(2)	107.7	H(21)-C(7) -H(20)	95.1
H(21)-C(7) -C(11)	111.4	H(21)-C(7) -S(3)	113.5
H(20)-C(7) -C(11)	109.6	H(20)-C(7) -S(3)	110.9
H(22)-C(8) -H(23)	121.9	H(22)-C(8) -C(17)	111.5
H(22)-C(8) -S(2)	106.6	H(23)-C(8) -C(17)	111.4
H(23)-C(8) -S(2)	93.8	H(24)-C(9) -H(25)	96.5
H(24)-C(9) -C(6)	109.7	H(24)-C(9) -S(4)	117.7
H(25)-C(9) -C(6)	109.3	H(25)-C(9) -S(4)	104.5
H(26)-C(10)-H(27)	98.7	H(26)-C(10)-C(14)	104.8
H(26)-C(10)-S(3)	115.7	H(27)-C(10)-C(14)	103.8
H(27)-C(10)-S(3)	114.3	H(29)-C(11)-H(28)	104.9
H(29)-C(11)-C(7)	104.1	H(29)-C(11)-S(5)	108.3
H(28)-C(11)-C(7)	106.9	H(28)-C(11)-S(5)	115.0
H(31)-C(12)-H(30)	94.1	H(31)-C(12)-C(13)	115.8
H(31)-C(12)-S(4)	113.1	H(30)-C(12)-C(13)	107.8
H(30)-C(12)-S(4)	108.7	H(33)-C(13)-H(32)	85.6
H(33)-C(13)-H(34)	121.1	H(33)-C(13)-C(12)	113.9
H(32)-C(13)-H(34)	126.8	H(32)-C(13)-C(12)	114.6
H(34)-C(13)-C(12)	96.2	H(35)-C(14)-H(37)	121.4
H(35)-C(14)-C(36)	73.8	H(35)-C(14)-C(10)	121.3
H(37)-C(14)-H(36)	156.6	H(37)-C(14)-C(10)	89.6
H(36)-C(14)-C(10)	96.9	H(39)-C(15)-H(38)	104.7
H(39)-C(15)-C(16)	115.2	H(39)-C(15)-S(5)	111.5
H(39)-C(15)-C(16)	109.0	H(38)-C(15)-S(5)	107.0
H(40)-C(16)-H(41)	84.8	H(40)-C(16)-H(42)	165.9
H(40)-C(16)-C(15)	97.3	H(41)-C(16)-H(42)	91.2
H(41)-C(16)-C(15)	102.5	H(42)-C(16)-C(15)	96.7
H(45)-C(17)-H(43)	111.2	H(45)-C(17)-H(44)	128.4
H(45)-C(17)-C(8)	100.46	H(43)-C(17)-H(44)	118.94
H(43)-C(17)-C(8)	83.3	H(44)-C(17)-C(8)	96.8

shown in Figure 8.

The Cu(I) ion is tetrahedrally surrounded by the four sulphur atoms from two ligand molecules, the Cu(I)-S distances being 2.280 ± 0.004Å, 2.303 ± 0.005Å, 2.310 ± 0.006Å and 2.318 ± 0.005Å. The average of these values (2.307Å) is very similar to the Cu(I)-S distances found in other structures as can be seen from Table XX. From this, it can be seen that Cu(I)-S distances of 2.3Å or greater are typical of tetrahedral stereochemistry, while trigonal Cu(I)-S distances seem to be approximately 0.05Å shorter. However, the Cu(I)-S distance found in $Cu(I)(DTO)_2BF_4$, and in all the other structures listed, is somewhat shorter than the predicted values based on the sum of the tetrahedral covalent radii of Cu(I), 1.35Å, and sulphur, 1.04Å i.e. 2.39Å(31). Such shortening suggests that some π bonding may be occurring i.e. a back donation of π electrons from the metal to the sulphur.

The tetrahedral angles about the Cu(I) ion vary from 94.0 to 121.1 degrees as shown in Table XVIII, this being presumably indicative of the magnitude of ring strain in the molecule. The average internal angle in the 2 five membered rings at Cu(I) is only 94.8 degrees, which is similar to those found in other comparable 5 membered rings, e.g. 92 degrees in the $Cu(I)(DTH)_2$dicarboxylic acid complex(58) and 90.2 degrees in the dimeric cyclic Cu(I)-aliphatic disulphide complex(57). Although tetrahedral Cu(I) complexes are apparently easily deformed, the range of S-Cu(I)-S angles in several other complexes is less e.g. 110-112 degrees in the sulphur bridged trigonal Cu(I)-trimer(66), 95-120 degrees in Decakis (thiourea) tetracopper (I) hexafluorosilicate monohydrate(70) and 104-112 degrees in tetrakis (thioacetamide) Cu(I) chloride(71). The large range of angles found in this structure is thus presumed to be due mainly to a chelate effect. Other indications of the amount of distortion in this complex are given by the dihedral angles between planes 1 and 2 (84.72 degrees) and planes 3 and 4 (102.08 degrees). The atoms defining these planes are shown in Table XXI.

The C-S distances average 1.805 ± 0.005Å when the S(8)-C(8) bond is not included. This bond has a length of

TABLE XX - COMPARISON OF Cu(I)-S BOND LENGTHS FOUND IN $Cu(I)(DTO)_2BF_4$ WITH THOSE OF OTHER STRUCTURES

COMPOUND	FORMULA	STEREO-CHEMISTRY	Cu(I)-S DISTANCE(Å)	REF.
cyclo di-μ{bis[2-(N,N-dimethylamino)ethyl] disulphide} dicopper(I)tetrafluoroborate	$Cu(I)_2(C_8H_{20}N_2S_2)_2(BF_4)_2$	Tetrahedral	2.30	(57)
decakis(thiourea)tetracopper(I)hexafluoro-silicate mono hydrate	$Cu(I)_4[SC(NH_2)_2]_{10}(SiF_6)_2\ H_2O$	Tetrahedral	2.315	(70)
Copper(I)2,5-dithiahexane-1,6-dicarboxylic acid	$Cu(I)^+[O_2C.CH_2.SCH_2.CH_2.SCH_2.CO_2H]_2H^+$	Tetrahedral	2.30,2.34	(58)
tris thiourea copper(I)tetrafluoroborate	$Cu(I)_2[SC(NH_2)_2]_6^{2+}(BF_4^-)_2$	Tetrahedral	2.3	(63)
tris (S-dimethylthiourea)copper(I)tetra-fluoroborate	$Cu(I)(SC(NH)_2(CH_3)_2]_3^+$ BF_4^-			
tetrakis(thioacetamide)copper(I)chloride	$C_8H_{20}N_4S_4CuCl$	Tetrahedral	2.343	(71)
diethyldisulphide copper(I) chloride	$Cu(I)_2(Et\text{-}S\text{-}SEt)_2Cl_2^-$	Tetrahedral	2.34,2.40	(65)
cyclo-tris-μ-(trimethylphosphine sulphide)-trichloro copper(I)	$[Cu(I)(Me_3PS)Cl]_3$	Trigonal	2.27	(66)
tris(ethylene thiourea)copper(I)sulphate	$Cu(I)(SC(NH)_2(CH_2)_2)_3^+(SO_4^{2-})_{\frac{1}{2}}$	Trigonal	2.28	(68)
tris(tetramethylthiourea)copper(I)tetra-fluoroborate	$Cu(I)(SC(N(CH_3)_2)_2)_3$ BF_4			
tris(trimethylphosphine sulphide)copper(I) perchlorate	$Cu(I)(SPMe_3)_3ClO_4$	Trigonal	2.26	(67)

TABLE XX (Continued)

COMPOUND	FORMULA	STEREO-CHEMISTRY	Cu(I)-2 DISTANCE(Å)	REF.
chlorobis-(2-thiouracil)copper(I)dimethyl formamide solvate	$ClCu(I)(SN_2C_4O_2)_2$ $HCON(CH_3)_2$	Trigonal	2.23	(69)
bis-(3,6-dithiaoctane)copper(I) tetrafluoroborate	$Cu(I)(CH_3CH_2SCH_2$ CH_2S- $CH_2CH_3)_2BF_4$	Tetrahedral	2.307	This work

1.87 ± 0.02Å, and hence is significantly longer than the others. There was no obvious reason for this lengthening, although it may be linked with the slightly shorter Cu(I)-S(2) bond. It is possible that the position of this sulphur may represent the mean of two extremes of vibration. However, it should be noted that these differences in bond lengths although significant, are quite small. Thus the carbon-sulphur bond lengths represent essentially single bonds, and are similar to those found in many other complexes including $Cu(II)(DTH)_2(BF_4)_2$, tetracarbonyl-dithiaoctane chromium(47), cyclo-di-μ {bis[2-(N,N-dimethyl-amino)ethyl]disulphide} dicopper(I) tetrafluoroborate(57), copper(I), 2,5-dithiahexane-1,6-dicarboxylic acid(58) and tetrakis(thioacetamide) copper(I) chloride(71). The C-S-C bond angles are all approximately tetrahedral as in the $Cu(II)(DTH)_2(BF_4)_2$ structure, but the Cu-S-C angles are considerably less at 96.1, 97.0, 97.1 and 93.3 degrees. Such distortion within the ring could be due to ring strain but is more likely to arise from some repulsion between the sp^3 hybrid orbitals, caused by the possible π back donation from the metal to the sulphur orbitals. Similar Cu-S-C bond angles have been found in the structure of Cu(I)2,5-dithiahexane-1,6-dicarboxylic acid (98 and 100 degrees) but not in the $Cu(II)(DTH)_2(BF_4)_2$ structure where there is little evidence of π back donation and in which the Cu-S-C angles are approximately tetrahedral.

The C-C bond lengths found in this structure vary from 1.44Å to 1.56Å as shown in Table XV, the distances being significantly different. The C-C bond distance of 1.44 ± 0.02Å within one of the 5 membered rings (C(7)-C(11)), is significantly shorter than the same bond in the other ring (C(6)-C(9))at 1.55 ± 0.02Å. This may be due to the close approach of 2.94Å between F[(52)IV] and C[(7)I] and the associated H[(20)I]-F[(52)IV] distance of 2.25Å which is considerably shorter than the sum of the van der Waal's radii of H and F (2.55Å). Although the presence of C-H----F hydrogen bonds is unlikely in the ordinary sense, the short C-H----F distance probably represents a polar attraction between the atoms(73,74) which could have an effect on the C(7)-C(11) bond. Similarly the other short

C-C bonds, C(10)-C(14) [1.45 ± 0.02Å], C(12)-C(13) [1.47 ± 0.02Å] are all associated with methyl hydrogens involved in short intermolecular contacts, e.g. H(33) and H(34) of C(13), and H(36) of C(14).(Table XVII). Other similar C-C distances have been reported e.g. 1.46 - 1.48Å (57). All the carbon atoms appear to be sp^3 hybridized as expected, since their stereochemistry is approximately tetrahedral. The C-C-S bond angles of the rings are almost identical to those found in the structures of copper(I) 2,5-dithiahexane-1,6-dicarboxylic acid(58) and cyclo-di-μ {bis[2-(N,N-dimethylamino)ethyl]disulphide} dicopper(I) tetrafluoroborate(57).

The two independent five membered rings $\overline{\text{Cu-S-C-C-S}}$ in the molecule are both in a gauche conformation, with one carbon atom above the plane formed by the Cu(I) and the two S atoms, and one below. The exact distances of these carbon atoms from the planes described are shown in Table XXI, where other mean plane calculations are also shown(28).

The C-H bond lengths were not unusual, most of the shorter ones being involved in short intermolecular contacts. There was some distortion in the tetrahedral stereochemistry of the methyl groups which has also been attributed to such contacts, although such distortion is not unusual, especially in terminal methyl groups(72), (Tables XVI and XIX).

The BF_4^- anion has already been discussed in detail in the section dealing with the refinement of the structure. The group had a strict tetrahedral geometry imposed on it by the rigid group restrictions, and was found to be disordered as shown in Figure 6. The B-F bond was shorter than expected at 1.34Å. This decrease in length can be attributed, as in the first structure, to increased π overlap between the empty 2p orbitals of the boron and the full 2p orbitals of the fluorine(44) or to the ionic character of the bond which may result due to the electronegativity difference between B and F. It is similar however to B-F bond distances found in other free BF_4^- ions, e.g. 1.18-1.42Å in [Cu(I))$_2$ $(C_8H_{20}N_2S_2)_2(BF_4)_2$](57) and 1.22Å-1.37Å in tris(thiourea) Cu(I)BF_4 and tris(S-dimethylthiourea) Cu(I)BF_4(63).

TABLE XXI - RESULTS OF MEAN PLANE CALCULATIONS

Plane	Atoms Defining Plane	Distance of Given Atoms from Plane
1	Cu(1) S(2) S(4)	C(6) 0.4755Å C(9) -0.2564Å
2	Cu(1) S(3) S(5)	C(7) 0.1467Å C(11) -0.4715Å
3	Cu(1) S(2) S(5)	
4	Cu(1) S(3) S(4)	

Angles between the normals to the planes

Plane	Plane	Angle (degrees)
1	2	84.72
3	4	102.08

Equations of Planes

1 $0.2226x + 0.8512y - 0.4752z + 0.3312 = 0$

2 $0.9198x - 0.2837y - 0.2711z - 1.9438 = 0$

3 $0.2459x - 0.8615y - 0.4442z + 0.8148 = 0$

4 $-0.5478x + 0.4502y - 0.7052z + 3.4772 = 0$

CHAPTER V

Conclusion

Structural models of copper-protein interaction have so far been related to a great extent to the co-ordination chemistry of low molecular weight complexes, because only one complete X-ray structure analysis of a "non blue" copper protein(59) has yet been achieved. As the cuprous ion favours a tetrahedral stereochemistry, and the cupric ion a square planar or octahedral one, and both are likely to show differences in their bonding requirements, the co-ordination environment of a copper ion in redox proteins is likely to be of an intermediate form, depending on its biological function(75). For this reason, it should be of great interest to compare the co-ordination spheres of a Cu(I) and Cu(II) complex with essentially the same ligand system. Such comparisons are not common, because of the marked specificity of these two metal ions for different ligands under inorganic conditions(13). Thus although the stereochemistries of simple inorganic complexes of Cu(I) and Cu(II) are expected to be different, valuable information about bond type and length for ligand co-ordination to two oxidation states may be obtained. This in turn, may be related to possible ligand co-ordination in redox proteins, especially if the ligand is similar to a biological ligand.

In this study, the structures of a Cu(I) and Cu(II) complex with methionine-like ligands were determined. The Cu(I) complex, $Cu(I)(DTO)_2BF_4$ had distorted tetrahedral co-ordination, while the Cu(II) complex $Cu(II)(DTH)_2(BF_4)_2$ was a tetragonally distorted octahedron. However, it was found that the Cu-S distances in both complexes were the same within experimental error. When considering the different ionic radii for the Cu(I) and Cu(II) ions [1.35Å and 1.30Å respectively], such equality is unexpected. The shortening in the Cu(I)-S bond is presumably due to some back donation of π electrons from the metal ion to the sulphur. This explanation is reinforced by comparing the predicted metal-sulphur bond distances with those found in the complexes $Cr(O)(CO)_4CTO$(47) $Cu(I)(DTO)_2BF_4$ and $Cu(II)(DTH)_2(BF_4)_2$. It is apparent that as the oxidation state of the metal decreases, the metal-S

distance also decreases compared to the predicted single bond distance. Hence virtually no shortening is observed in the Cu(II)-S bond [2.317Å cf. 2.34Å], while some occurs in the Cu(I)-S bond [2.307Å cf. 2.39Å] and even more in the Cr(0)-S bond where the bond length is 2.42Å compared to a predicted length of 2.52Å. As a decrease in bond length can be related to an increase in metal → ligand π donation(79), it must also be related to the ability of the metal ion to donate π electrons to the ligand. Thus complexes involving π acceptor ligands are usually only found with metal ions of low positive, zero, or low negative oxidation states (79) i.e. Cr(0) and Cu(I).

π acceptor ligands must be able to act as σ donors and π acceptors, which means they must have both vacant orbitals and lone pairs. Included in this class of ligands are molecules like R_2S, and those with delocalised π orbitals such as thiourea(34). The structures of a Cu(I) and Cu(II) complex with thiourea ligands have been determined. They are bis(thiourea) Cu(I) chloride, and dichlorobis(tetra methylthiourea)Cu(II)(78,34). In the Cu(I) complex there are two distinct types of Cu-S bond. Two of these bonds average 2.25Å and are characteristic of trigonal bonds, while the other is 2.31Å and is characteristic of a tetrahedral bond(63). However, both these distances are much shorter than the predicted 2.39Å, indicating the presence of some π bonding. The Cu(II) complex on the other hand, is made up of isolated molecules containing chlorine and sulphur ligands with a conformation intermediate between tetrahedral and square planar, and Cu(II)-S distances of 2.32Å and 2.31Å. These are almost the same as the predicted Cu(II)-S bond length [2.34Å] and are very similar to the distances found in $Cu(II)(DTH)_2(BF_4)_2$, representing a strong covalent single bond(84,85). Again the similarity in bond lengths can be seen between the tetrahedral-like Cu-S bonds in both the Cu(I) and Cu(II) complex.

Having established the differences in bonding to Cu(I) and Cu(II) by sulphur ligands of the type mentioned above, it is of interest to compare other ligands of biological significance. Two complexes which allow a close comparison are tetrakis imidazol copper(II) iodide(76) and tetrapyridine

copper(I) perchlorate(77). Imidazole ligands are biologically important, and pyridine is expected to be similar in its co-ordination properties. In the Cu(I) tetrapyridine structure, the Cu(I)-N distance is 2.05 ± 0.01Å compared to a predicted bond length of 2.05Å, and the co-ordination is tetrahedral. For the Cu(II) complex, the Cu(II)-N bonds average 2.01 ± 0.02Å compared to a predicted value of 2.00Å and the co-ordination is square planar. Hence, in both complexes, the Cu-N bond is essentially a single covalent bond, and presumably this reflects the fact that these ligands are not good enough π acceptors to shorten the Cu(I)-N bonds.

In an electron transfer protein, rapid transfer of the electron is facilitated if structural changes are small. On the other hand, electron transfer may not be possible without some movement of atoms or groups of atoms, and such movements may be required to be in specific directions. Thus the observed bond lengths in Cu(I) and Cu(II) complexes may be of direct relevance to the electron transfer process in Cu-proteins. In the Cu(I) and Cu(II) thioether complexes, no change in bond length is observed as the metal changes its oxidation state. On the other hand, in Cu(I) and Cu(II) complexes with imidazole type ligands there is a small change in bond length (the differences between the two types of ligand being attributed to their different π acceptor characteristics). Of course the effect on the bond lengths of the different stereochemistries in the Cu(I) and Cu(II) complexes is difficult to estimate. Nevertheless, the above results suggest that where a Cu atom is co-ordinated to both N and S ligands in a protein, the lengths of the Cu-S bonds may be unaffected by change in the oxidation state of the Cu (i.e. by the electron transfer process) but that the length of the Cu-N bonds may change, thus allowing small structural changes to be transmitted in a particular direction.

BIBLIOGRAPHY

(1) Maugh, T.H. Science, 187, 154-156 (1975).

(2) Malkin, R. and Malmström, B.G. Advances in Enzymology, 33, 177 (1970).

(3) Sigwart, C., et al., Inorganic Chemistry, 7-12, 2545 (1968).

(4) Osterberg, R. Co-ordination Chemistry Reviews, 12, 309-347 (1974).

(5) Hemmerich, P. in Peisach, J. et al., eds. The Biochemistry of Copper, Academic Press, New York (1966), pp. 15-34.

(6) Williams, R.J.P. Biochemical Society Transactions, 1, 1-25 (1973).

(7) McMillin, D.R., et al., Proceedings of the National Academy of Science, 71:4, 1339-1341 (1974).

(8) McMillin, D.R., et al., Proceedings of the National Academy of Science, 71:12, 4760-4762 (1974).

(9) Blumberg, W.E. in Peisach, J., et al., eds. The Biochemistry of Copper, Academic Press, New York (1966), pp. 49-65.

(10) Klotz, I.M., et al. Journal of the American Chemical Society, 80, 553 (1952).

(11) Beinert, H. in Peisach, J., et al., eds. The Biochemistry of Copper, Academic Press, New York (1966), pp. 215-234.

(12) Pearson, R.G. Journal of the American Chemical Society, 85, 3533 (1963).

(13) Sigel, H. and McCormich, D.B. Accounts of Chemical Research, 3, 201-208 (1970).

(14) Temussi, P.A. and Vitagliano, A. Journal of the American Chemical Society, 97:6 (1975).

(15) Freeman, H.C. Advances in Protein Chemistry, 22, 257-424 (1967).

(16) Freeman, H.C. in Peisach, J. et al., eds. The Biochemistry of Copper, Academic Press, New York (1966), p. 77.

(17) Hatfield, W.E. and Whyman, R. Transition Metal Chemistry, 5, 47-179 (1967).

(18) Ali, M.A. and Livingstone, S.E. Co-ordination Chemistry Reviews, 13, 101-132 (1974).

(19) Hall, D.O. Nature, 255, 578-579 (1975).

(20) Holm, R.H. Endeavor XXXIV:121, 38-43 (1975).

(21) Bergen, H.A. Report, B.Sc. Hons., Massey University (1973) 36p.

(22) Palmer, K. Thesis, M.Sc., Massey University (1975).

(23) Stout, G.H. and Jensen, L.H. X-Ray Structure Determination, a Practical Guide. Collier Macmillan Ltd., London (1968).

(24) International Tables for X-Ray Crystallography, Vol. III, pp. 202-212.

(25) FOURIER. A rewritten and expanded version of the program FORDAP (by A. Zalkin) written by R.J. Dellaca, Canterbury University.

(26) CUCLS. A modified version of ORFLS (by Busing and Levy) written by R.J. Dellaca, Canterbury University.

(27) DANTEP. A modified version of ORTEP (by C. Johnson) written by R.J. Dellaca, Canterbury University.

(28) CORFFE. A modified version of ORFFE (by Busing and Levy) written by R.J. Dellaca, Canterbury University.

(29) MEAN PLANE. A program written by Pippy, M.E. and Ahmed, F.R., Division of Pure Physics, National Research Council, Ottawa.

(30) RBANG. A program written by S.F. Watkins, at the University of Wisconsin with minor modification. University of Canterbury.

(31) Pauling, L., The Nature of the Chemical Bond, Third Ed., Cornell University Press, New York (1960).

(32) Hathaway, B.S. and Billing, D.F. Co-ordination Chemistry Reviews, 5, 143-207 (1970).

(33) Brown, D.S., et al., Acta Crystallographica, B.24, 730-734 (1968).

(34) Spofford, W.A., et al. Chemical Communications, 533-534, (1970).

(35) Hoskins, B.F. and Whillans, F.P. Chemical Society Journal, Dalton Transactions, 2112-2116 (1974).

(36) Ferrari, M.B., et al., Acta Crystallographica, B29:9 1808 (1973).

(37) Newman, P.W.G., et al., Chemical Society Journal, Dalton Transactions, 1332-1335 (1973).

(38) Martin, J.M., et al., Chemical Society Journal, Dalton Transactions, 2233-2237 (1972).

(39) Villa, A.C., et al. Crystal Structure Communications, 1, 207 (1972).

(40) Villa, A.C., et al. Crystal Structure Communications, 1, 125 (1972).

(41) Peyronel, G., et al. Acta Crystallographica, B28, 3596 (1972).

(42) Solomon, E.I., et al. Journal of the American Chemical Society, 97:13, 3878-3879 (1975).

(43) Gray, H.B. Electrons and Chemical Bonding, W.A. Benjamin Inc., New York (1965).

(44) Pettit, L.D. Quarterly Reviews of the Chemical Society, 25:1, 1-29 (1971).

(45) Cruickshank, D.W.J. Acta Crystallographica, 9, 757 (1956).

(46) Cruickshank, D.W.J. Acta Crystallographica, 9, 754 (1956).

(47) Larsen, N. B.Sc.Hons. Report, Massey University (1975).

(48) De Simone, R.E. and Glick, M.D. Journal of the American Chemical Society, 97:4, 942-943 (1975).

(49) Richardson, J.S., et al. Proceedings of the National Academy of Sciences, 72:4, 1349-1353 (1975).

(50) Dickerson, R.E., et al. Journal of Biological Chemistry, 246:5, 1511-1535 (1971).

(51) Busing, W.R. and Levy, H.A. Acta Crystallographica, 17, 142 (1964).

(52) Drew, G.B. and Riedl, M.J. Chemical Society Journal, Dalton Transactions, 52-55 (1973).

(53) Cotton, F.A. and Weaver, D.L. Journal of the American Chemical Society, 87:18, 4190 (1965).

(54) Bonamico, M., et al. Acta Crystallographica, 19, 886 (1965).

(55) Pignedoli, A. and Peyronel, G. Gazzetta, 72, 745 (1962).

(56) Dalley, N.K., et al. Chemical Society Journal, Chemical Communications, 3, 84-86 (1975).

(57) Otterson, T., et al. Inorganic Chemistry, 13:8, 1904-1911 (1974).

(58) van der Meer, H. Chemical Society Journal, Dalton Transactions, 1-2 (1973).

(59) Azaroff, L.V. Elements of X-ray Crystallography, McGraw-Hill Book Company, 1968, p. 309.

(60) Baily, M.F. and Dahl, L.F. Inorganic Chemistry, 9, 1306-1314 (1965).

(61) Doedens, R.J. Group Least Squares Refinement in Crystallographic Computing. F.R. Ahmed, Ed. Munksgaard (1970).

(62) Scheringer, C. Acta Crystallographica, 16, 546 (1963).

(63) Taylor, I.F., et al. Inorganic Chemistry, 13, 2835-2841 (1974).

(64) Churchill, M.R. and Kalru, K.L. Inorganic Chemistry, 13, 1427 (1974).

(65) Branden, C.I. Acta. Chem. Scand., 21, 1000 (1967).

(66) Tiethoff, J.A., et al. Chemical Society Journal Chemical Communications, 1141-1142 (1972).

(67) Eller, P.G. and Corfield, P.W.R. Chemical Society Journal Chemical Communications, 105 (1971).

(68) Weininger, M.S., et al. Chemical Society Journal Chemical Communications, 1140-1141 (1972).

(69) Hunt, G.W. and Amma, E.L. Chemical Society Journal Chemical Communications 869-870 (1973).

(70) Gash, A.G., et al. Chemical Society Journal Chemical Communications, 256 (1973).

(71) Truter, M.R. and Rutherford, K.W. Chemical Society Journal, 1748 (1962).

(72) Kitaigorodskii, Press of the Academy of Sciences of the U.S.S.R. in Moscow (1955).

(73) Sutor, D.J. Nature, 68, (1962).

(74) Larsson, K. Arkiv för Kemi Band 23 nr 1.

(75) Williams, R.J.P. Royal Institute of Chemistry Reviews, 1, 13 (1968).

(76) Akhtar, F., et al. The Chemical Society Journal Chemical Communications, 1400-1401 (1971).

(78) Spofford, W.A. and Amma, E.L. Chemical Society Journal Chemical Communications, 7, 405-408 (1968).

(79) Cotton, F.A. and Wilkinson, G. Advanced Inorganic Chemistry, Interscience Publishers, New York, 2nd Ed. (1966).

(80) Macbeath, A.M. Elementary Vector Algebra, Oxford University Press (1964), p. 55.

(81) HILGOUT. A computer program written by R.J. Dellaca, Canterbury University.

(82) Brill, A.S., *et al.* *in* B. Pullman (Ed.) Electronic Aspects of Biochemistry, Academic Press, New York (1964), p. 519.

(83) Heslop, R.B. and Robinson, P.L. Inorganic Chemistry, Elsvier Publishing Company, London (1961), p. 494.

(84) Campbell, M.J.M. Co-ordination Chemistry Reviews, 15, 279-319 (1975).

(85) Buluggia, E., *et al.* Journal of Chemical Physics, 56:11, 5602-6 (1972).

APPENDIX 1

Structure Factor Tables for $Cu(II)(DTH)_2(BF_4)_2$

H	K	L	Y(OBS)	Y(CALC)
1	0	0	95.60	86.81
2	0	0	61.70	57.38
3	0	0	70.37	68.15
4	0	0	51.10	52.78
5	0	0	23.07	23.88
6	0	0	15.49	16.04
7	0	0	30.59	28.81
8	0	0	10.49	10.16
1	1	0	34.03	29.31
2	1	0	11.65	10.75
3	1	0	15.13	14.72
4	1	0	32.90	30.94
5	1	0	9.14	7.96
0	2	0	81.23	79.08
1	2	0	106.32	103.40
2	2	0	32.60	29.93
3	2	0	63.75	62.11
4	2	0	52.18	49.47
7	2	0	6.16	5.40
8	2	0	7.69	7.02
1	3	0	81.65	79.30
2	3	0	26.33	25.47
3	3	0	37.81	34.67
4	3	0	23.85	24.07
5	3	0	16.59	17.28
6	3	0	18.82	19.75
7	3	0	11.06	12.05
0	4	0	124.30	124.84
1	4	0	29.22	28.93
2	4	0	24.01	22.54
3	4	0	37.22	37.57
4	4	0	20.18	20.16
5	4	0	10.28	8.70
6	4	0	12.32	14.36
7	4	0	17.95	18.47
8	4	0	6.54	7.12
1	5	0	17.20	13.92
2	5	0	15.11	15.76
4	5	0	31.14	31.02
5	5	0	15.09	14.08
6	5	0	6.15	7.90
7	5	0	8.96	8.18
0	6	0	45.64	41.20
1	6	0	20.15	20.90
2	6	0	50.37	51.40
3	6	0	23.50	24.83
4	6	0	11.87	10.99
5	6	0	30.75	29.65
6	6	0	26.43	26.50
1	7	0	10.93	10.88
2	7	0	8.95	10.15
3	7	0	10.48	10.93
0	-8	0	7.07	3.70
1	8	0	5.02	6.16
2	8	0	25.45	25.64
3	8	0	13.46	15.13
4	8	0	8.82	9.91
5	8	0	22.54	21.53
6	8	0	20.09	20.27
3	9	0	5.46	3.38
4	9	0	4.82	4.27
1	10	0	6.42	7.04
2	10	0	10.15	12.04
3	10	0	7.97	9.58
4	10	0	9.73	9.95
5	10	0	13.93	13.49
1	11	0	10.30	10.04
0	-12	0	8.95	10.56
1	12	0	4.55	6.16
0	1	1	99.26	99.02
1	1	-1	75.20	74.55
1	1	1	52.51	48.61
2	1	-1	47.76	48.14
2	1	1	14.95	12.41
3	1	-1	89.06	87.20
3	1	1	23.56	23.75
4	1	-1	68.42	66.84
4	1	1	18.19	16.96
5	1	1	7.54	8.00
6	1	1	16.56	16.36
7	1	-1	22.24	21.40
7	1	1	25.28	24.58
8	1	-1	5.06	6.92
8	1	1	17.00	16.13
0	2	1	33.17	26.48
1	2	-1	69.20	64.99
1	2	1	84.68	78.92
2	2	-1	17.24	19.69
3	2	-1	33.61	33.66
3	2	1	36.37	35.64
4	2	-1	25.68	25.92
4	2	1	6.13	6.48
5	2	-1	33.83	33.75
5	2	1	9.04	9.26
6	2	1	21.00	19.93
7	2	-1	4.22	4.16
7	2	1	9.59	8.92
8	2	-1	6.76	6.60
8	2	1	6.07	4.04
0	-3	-1	64.91	60.54
1	3	-1	63.20	55.96
1	3	1	19.79	21.24
2	3	-1	23.23	22.10
2	3	1	42.51	41.82
3	3	-1	54.83	58.72
3	3	1	29.77	29.90
4	3	-1	49.16	50.38
4	3	1	28.09	28.30
5	3	-1	20.83	21.95
5	3	1	16.72	14.28
6	3	-1	6.54	6.62
6	3	1	12.23	13.52
7	3	-1	15.47	15.83
7	3	1	15.09	15.67
8	3	-1	9.06	9.47
8	3	1	11.02	9.61
0	-4	-1	16.13	17.74
1	4	-1	27.10	26.52
1	4	1	95.13	94.08
2	4	1	22.42	21.01
3	-4	-1	15.59	15.56
3	4	1	32.81	29.54
4	4	-1	29.03	26.25
5	4	-1	28.42	28.98
5	4	1	3.70	3.81
6	4	1	19.44	17.37
7	4	1	12.01	12.52
0	5	-1	25.25	26.82
1	5	-1	46.98	46.74
2	5	-1	43.25	42.99
3	5	-1	37.74	37.42
4	5	-1	36.07	35.85
4	5	1	4.81	2.75
5	5	-1	25.68	25.31
5	5	1	15.43	14.43
6	5	-1	14.16	13.19
6	5	1	20.53	20.29
7	5	-1	27.82	29.33
7	5	1	21.46	23.40
8	5	1	18.39	19.17
1	6	-1	12.27	11.41
1	6	1	3.94	2.23
0	6	1	19.84	18.92
1	6	-1	16.49	16.09
1	6	1	27.38	27.10
2	6	-1	21.13	21.85
3	6	-1	14.11	14.75
3	6	1	18.18	13.41
4	6	-1	19.25	17.56
5	6	-1	19.04	17.71
5	6	1	4.82	4.03
6	6	1	14.79	14.65
7	6	1	6.24	4.87
0	7	1	7.58	7.80
1	7	-1	20.94	19.75
1	7	1	17.44	18.16
2	7	-1	12.64	10.12
2	7	1	47.48	48.20
3	7	1	26.21	27.26
4	7	-1	9.37	8.02
4	7	1	21.75	23.18
5	7	-1	31.02	29.35
5	7	1	23.31	23.78
6	7	-1	15.81	15.88
6	7	1	9.94	11.42
0	-8	-1	4.52	4.97
1	-8	-1	13.35	13.41
2	8	1	8.09	8.00
3	8	-1	10.08	10.05
3	8	1	4.06	3.61
4	8	1	8.17	5.13
5	8	-1	5.65	5.77
5	8	1	6.93	6.01
0	-9	-1	7.92	7.99
1	-9	-1	15.72	14.59
1	9	1	19.62	19.75
2	9	-1	12.46	11.70
2	9	1	24.48	24.98
3	9	1	16.43	18.42
4	9	-1	3.99	2.86
4	9	1	9.06	10.79
5	9	-1	13.16	11.56
5	9	1	15.69	16.21
6	9	-1	12.87	12.90
6	10	1	6.65	7.67
1	-10	-1	7.79	6.18
1	10	1	15.16	16.00
2	10	-1	6.09	4.50
3	10	-1	6.05	5.45
3	10	1	5.02	4.42
4	10	-1	4.48	4.39
4	10	1	7.69	8.91
1	-11	-1	5.49	5.40
1	11	-1	6.39	6.83
2	11	1	9.84	10.16
2	11	-1	6.69	7.08
2	11	1	15.50	14.86
3	11	1	10.39	9.77
4	11	-1	5.72	5.64
0	-12	-1	5.34	5.67
1	12	1	6.78	8.34
0	0	2	85.95	88.38
1	0	-2	53.12	45.93
1	0	2	35.98	31.11
2	0	-2	51.27	50.30
2	0	2	81.72	82.41
3	0	-2	100.53	100.14
3	0	2	14.82	14.94
4	0	-2	83.49	84.74
4	0	2	66.46	65.09
5	0	-2	31.72	29.99
5	0	2	9.74	11.14
6	0	-2	17.39	15.71
6	0	2	26.54	29.30
7	0	-2	36.08	35.47
7	0	2	35.26	35.09
8	0	-2	22.25	22.91
8	0	2	15.50	15.74
0	-1	-2	50.43	45.84
1	1	-2	20.91	22.65
2	1	-2	52.11	47.06
2	1	2	36.23	37.99
3	1	-2	43.89	37.69
4	1	-2	15.30	15.22
5	1	-2	16.27	12.37
6	1	-2	7.96	7.41
7	1	-2	10.76	10.57
7	1	2	4.73	4.50
8	1	-2	9.82	10.88
0	-2	-2	20.44	21.90
1	-2	-2	36.00	34.09
1	2	2	36.96	34.60
2	2	-2	65.33	67.89
2	2	2	15.13	18.77
3	2	-2	32.16	29.25
3	2	2	29.70	29.67
4	-2	-2	75.68	69.67
4	2	2	35.54	35.66
5	2	-2	52.38	53.97
5	2	2	32.79	33.75
6	2	-2	34.64	36.46
6	2	2	10.28	9.84
7	2	-2	25.45	25.35
7	2	2	20.38	20.65
8	2	-2	8.78	8.54
0	-3	-2	29.26	29.22
1	3	2	22.44	22.03
2	3	-2	74.24	74.84
3	3	-2	39.54	39.92
3	3	2	48.36	48.36
4	3	-2	33.85	34.30
4	3	2	14.50	13.21
5	3	2	13.11	13.40
6	3	-2	11.72	11.99
6	3	2	16.44	16.58
8	3	-2	16.21	15.99
0	-4	-2	50.67	46.93
1	-4	-2	47.55	44.72
4	4	2	37.27	37.64
5	4	-2	30.18	30.89
2	4	2	18.91	18.11
3	4	-2	59.63	59.65
3	4	2	13.78	13.80
5	4	-2	15.66	16.76
6	4	2	26.83	27.73
7	5	-2	17.75	17.99
5	4	2	16.50	17.21
6	4	-2	18.64	18.12
6	4	2	19.08	19.12
7	4	-2	16.64	15.15
7	4	2	11.63	11.05
8	4	-2	12.65	12.80
0	-5	-2	4.44	4.61
1	-5	-2	14.97	13.44
1	5	2	9.31	8.56
2	5	-2	42.97	42.81
2	5	2	28.90	29.06
3	5	-2	47.54	45.40
3	5	2	21.53	18.18
4	5	2	6.60	4.96
5	5	-2	13.69	12.66
6	5	-2	12.10	10.43
6	5	2	11.33	11.81
7	5	-2	7.48	7.33
8	5	-2	15.63	16.17
0	6	2	5.41	5.29
1	-6	-2	24.33	22.57
1	-6	2	58.51	58.88
2	6	-2	67.24	66.07
2	6	2	66.48	66.29
3	6	-2	4.16	3.70
3	6	2	15.84	14.93
4	6	-2	3.36	4.94
5	6	-2	19.49	21.46
5	6	2	22.11	21.48
6	6	-2	20.51	21.50
8	6	-2	5.81	6.43
0	7	2	4.52	5.74
1	7	2	5.95	3.75
2	7	-2	18.43	19.30
3	7	-2	5.37	4.93
3	7	2	10.55	10.83
4	7	-2	5.07	3.86
4	7	2	8.67	8.09
5	7	-2	6.14	3.61
5	7	2	6.89	5.60
0	8	2	22.01	18.55
1	-8	-2	23.71	21.24
1	8	2	43.09	39.63
2	8	-2	32.18	32.57
2	8	2	38.90	36.50
3	8	-2	15.18	13.34
3	8	2	10.21	9.77
4	8	-2	7.93	7.79
5	8	-2	7.49	7.97
5	8	2	10.52	11.95
6	8	-2	7.87	9.08
0	-9	-2	4.26	3.37
2	9	-2	10.68	10.19
4	9	-2	5.27	5.68
0	-10	-2	13.96	11.68
1	-10	-2	21.68	18.82
1	10	2	20.11	20.05
2	10	-2	19.60	17.20
2	10	2	20.78	20.52
3	10	2	10.41	9.27
5	10	-2	6.78	8.08
0	11	2	4.01	3.12
1	11	-2	5.52	5.50
1	11	2	8.54	8.94
2	11	-2	7.50	6.68
2	12	2	13.25	11.65
1	-12	-2	9.17	7.85
0	-1	-3	51.80	49.33
1	-1	-3	38.49	39.97
1	1	3	36.93	38.58
2	1	3	15.17	16.83
3	1	-3	87.28	86.07
3	1	3	49.58	49.20
4	1	-3	54.78	50.61
4	1	3	50.00	49.73
5	1	-3	12.17	11.94
5	1	3	18.53	17.90
6	1	-3	35.80	35.40
6	1	3	15.75	15.65
7	1	-3	49.28	50.07
7	1	3	18.81	20.18
8	1	-3	20.36	21.28
8	1	3	4.25	3.73
8	2	-3	6.45	8.44
0	-2	-3	23.72	25.29
1	2	3	38.08	38.04
2	2	-3	59.30	62.07
2	2	3	25.02	26.06
3	2	-3	26.32	24.96
3	-2	3	17.67	16.96
4	2	3	8.78	7.78
4	2	-3	12.44	12.05
5	2	-3	6.10	3.83
5	2	3	11.72	12.14
6	2	-3	5.74	6.87
0	-3	-3	34.77	33.38
1	-3	-3	15.65	15.98
1	3	3	44.90	43.35
2	3	-3	20.11	17.53
3	3	3	28.37	27.25
3	-3	-3	41.07	39.41
4	3	3	42.76	44.77
4	3	-3	39.90	40.62
5	3	3	29.26	29.69
5	3	-3	27.80	27.58
6	3	3	11.72	12.23
6	3	-3	30.88	32.33
7	3	3	15.01	15.60
7	3	-3	25.07	24.22

7	3	3	12.46	12.37	1	3	4	17.51	19.52	3	4	5	7.77	7.00
8	3	-3	13.49	13.81	2	-3	-4	3.58	5.24	4	4	-5	30.35	31.77
9	3	-3	6.54	7.03	2	3	4	3.94	6.62	4	4	5	20.24	21.38
0	-4	-3	7.81	8.13	3	3	-4	8.04	8.71	5	-4	-5	19.54	19.99
1	-4	-3	32.41	32.69	3	3	4	6.34	7.49	5	4	5	8.11	9.26
1	4	3	10.73	8.36	4	-3	-4	37.55	37.07	6	4	-5	12.38	10.84
2	4	-3	13.38	16.35	4	3	4	19.26	21.03	6	4	5	10.21	9.75
2	4	3	35.51	35.69	5	3	-4	5.28	8.72	7	4	-5	11.90	13.04
3	4	-3	35.32	34.16	5	3	4	13.65	13.81	9	4	-5	8.21	8.71
3	4	3	28.15	29.11	6	3	-4	26.25	27.32	1	-5	5	29.25	32.61
4	4	-3	16.60	15.98	6	3	4	4.39	2.92	1	5	5	16.52	17.88
5	4	-3	6.46	4.48	7	3	-4	15.33	17.00	2	-5	-5	40.14	37.86
5	4	3	12.39	13.31	0	-4	-4	37.35	36.96	2	5	5	20.19	21.85
6	4	-3	20.11	19.65	1	-4	-4	37.66	36.75	3	-5	-5	25.35	25.95
8	4	-3	12.76	13.72	1	4	4	26.20	24.57	3	5	5	13.62	12.94
0	5	3	46.58	46.57	2	-4	-4	30.13	32.00	4	-5	-5	19.92	19.92
1	5	-3	46.11	42.94	2	4	4	20.35	19.32	4	5	5	15.82	14.96
1	5	3	24.83	25.25	3	4	-4	40.51	43.47	5	5	-5	28.18	28.12
2	5	-3	54.05	57.63	3	4	4	30.00	33.09	5	5	5	14.82	15.75
2	5	3	22.54	24.22	4	-4	-4	37.08	39.58	6	5	-5	24.74	24.88
3	5	-3	33.36	36.58	4	4	4	9.28	9.33	7	5	-5	10.08	9.64
3	5	3	10.66	9.43	5	4	-4	10.36	10.38	8	5	-5	7.77	9.01
4	5	-3	7.38	8.25	5	4	4	13.80	14.30	0	-6	-5	8.51	6.46
4	5	3	12.92	13.26	6	-4	-4	16.14	12.72	1	-6	-5	18.93	18.28
5	5	-3	17.68	20.01	6	4	4	13.08	13.63	1	6	5	16.14	18.36
5	5	3	17.29	17.11	7	4	-4	10.54	11.71	2	6	-5	15.62	15.92
6	5	-3	20.92	20.09	8	4	-4	9.82	10.16	3	6	-5	5.08	8.62
6	5	3	11.33	9.82	9	4	-4	8.82	8.80	3	6	5	9.67	9.35
7	5	-3	7.11	5.82	0	-5	-4	19.37	17.45	4	6	-5	6.04	4.95
0	-6	-3	9.33	8.34	1	-5	-4	49.97	51.55	4	6	5	11.42	10.78
1	6	-3	11.48	11.31	2	5	-4	12.03	13.34	5	6	-5	7.29	6.28
1	6	3	13.02	11.16	3	5	-4	3.49	3.94	6	6	-5	8.66	6.16
2	6	3	20.15	21.29	4	5	4	21.02	19.41	0	7	5	10.07	9.85
3	6	-3	31.81	33.40	5	5	4	15.25	14.56	1	-7	-5	12.28	12.40
3	6	3	9.03	11.15	6	5	-4	22.59	24.76	1	7	5	10.24	9.24
4	6	-3	14.89	13.69	7	5	-4	14.31	14.26	2	-7	-5	32.15	34.26
4	6	3	11.99	11.17	8	5	-4	6.20	5.40	2	7	5	25.31	27.15
5	6	-3	5.66	5.46	1	-6	-4	23.31	25.01	3	7	5	7.73	8.63
6	6	-3	9.82	8.78	1	6	4	21.00	22.90	4	7	-5	5.83	5.43
8	6	-3	8.18	7.23	2	-6	-4	48.18	50.82	4	7	5	4.74	5.73
0	7	3	18.89	19.37	2	6	4	31.02	33.54	5	7	-5	40.51	40.68
1	7	-3	48.52	46.62	3	-6	-4	27.24	26.05	6	7	-5	31.13	29.85
1	7	3	28.55	29.43	4	6	-4	15.61	14.70	7	7	-5	6.64	6.72
2	7	-3	41.15	43.10	5	6	-4	34.43	32.39	0	-8	-5	2.89	0.25
2	7	3	27.32	23.79	5	6	4	16.11	16.72	1	-8	-5	5.30	3.98
3	7	-3	10.90	10.77	6	6	-4	21.38	21.63	2	-8	-5	6.52	6.20
3	7	3	11.08	9.27	7	6	-4	7.76	5.48	4	8	-5	7.02	7.40
4	7	-3	9.29	10.56	0	7	4	12.54	13.01	0	-9	-5	5.69	6.50
5	7	-3	24.15	23.85	1	-7	-4	5.52	4.12	1	-9	-5	6.52	6.90
5	7	3	7.10	8.47	2	-7	-4	3.59	1.32	1	9	5	3.99	6.09
6	7	-3	12.47	14.56	2	7	4	4.72	2.37	2	-9	-5	15.26	14.29
6	7	3	7.51	7.03	3	-7	-4	4.07	4.01	2	9	5	10.54	12.76
7	7	-3	7.03	7.43	4	-7	-4	8.17	7.47	3	-9	-5	11.51	10.93
0	8	3	3.97	2.09	5	7	-4	8.25	7.42	3	9	5	7.45	6.86
1	8	-3	7.09	7.66	6	7	-4	6.09	5.00	4	9	-5	11.54	11.13
1	8	3	5.62	7.12	1	-8	-4	12.05	13.08	5	9	-5	20.71	19.84
3	8	-3	10.17	9.73	1	8	4	10.72	11.29	6	9	-5	17.56	16.25
4	8	3	9.14	7.65	2	-8	-4	27.54	28.88	1	-10	-5	5.92	5.32
0	-9	-3	20.37	20.37	2	8	4	6.09	8.23	1	10	5	4.01	4.20
1	9	-3	27.52	27.33	3	8	-4	30.30	33.48	2	-10	-5	6.22	5.90
1	9	3	14.28	14.28	4	-8	-4	22.65	23.92	4	-10	-5	5.78	4.75
2	9	-3	32.36	32.67	5	8	-4	18.82	19.32	5	10	-5	4.76	5.24
2	9	3	11.33	12.36	6	8	-4	17.10	14.88	0	-11	-5	4.80	4.92
3	9	-3	17.23	18.00	7	8	-4	4.81	3.10	2	-11	-5	5.50	6.63
4	9	-3	6.33	6.72	0	9	4	7.42	8.11	3	-11	-5	4.72	4.70
4	9	3	3.80	1.15	1	-9	-4	10.12	9.00	0	0	6	62.77	61.41
5	9	3	8.55	10.14	1	9	4	4.61	3.16	1	0	-6	37.17	33.27
1	-10	-3	7.99	8.55	2	-9	-4	6.01	7.21	1	0	6	11.59	13.44
1	10	3	8.45	5.22	3	9	-4	7.99	7.61	2	0	-6	26.90	31.67
2	10	3	6.40	7.74	4	9	-4	10.20	8.83	2	0	6	8.84	8.90
2	-10	3	7.95	7.79	6	9	-4	5.81	5.14	3	0	-6	75.69	79.16
3	10	-3	6.35	6.97	1	-10	-4	12.17	14.48	3	0	6	16.44	17.14
3	10	3	9.34	8.45	2	-10	-4	17.95	19.88	4	0	-6	70.00	67.94
0	-11	-3	10.62	10.09	2	10	4	5.90	8.26	4	0	6	17.72	18.26
1	-11	-3	11.14	11.20	3	10	-4	11.21	10.39	5	0	-6	31.21	30.21
1	11	3	11.62	11.83	4	10	-4	13.08	12.16	6	0	-6	14.21	10.99
2	-11	-3	10.69	11.99	5	10	-4	16.61	16.07	6	0	6	7.25	5.63
2	11	3	8.37	6.65	1	-11	-4	11.48	11.78	7	0	-6	15.90	15.89
3	11	-3	10.16	10.39	2	-11	-4	5.22	4.42	0	1	6	13.97	15.95
4	11	-3	8.89	8.13	0	1	5	92.74	92.52	1	-1	-6	14.88	17.97
0	0	4	121.99	118.69	1	-1	-5	72.25	72.06	1	1	6	27.56	26.07
1	0	-4	105.93	105.41	1	1	5	53.42	54.18	2	1	-6	19.60	23.76
1	0	4	18.83	17.33	2	1	-5	20.30	20.10	3	-1	-6	26.60	30.51
2	0	-4	7.57	6.09	2	1	5	20.57	21.25	3	1	6	9.75	10.57
2	0	4	22.13	20.88	3	1	-5	42.06	44.04	4	1	-6	5.95	6.26
3	0	-4	12.56	11.17	3	1	5	26.99	27.25	4	1	6	7.02	6.56
3	0	4	41.32	42.80	4	1	-5	44.85	45.32	5	-1	-6	21.60	20.06
4	0	-4	53.40	53.56	4	1	5	20.88	20.40	5	1	6	5.34	4.45
4	0	4	31.27	32.74	5	1	-5	9.56	9.82	6	1	-6	8.13	8.82
5	0	-4	11.20	9.48	6	-1	-5	14.29	15.91	6	1	6	6.51	6.00
6	0	4	5.23	6.51	7	1	-5	17.31	16.40	7	1	-6	13.01	9.82
7	0	-4	25.74	27.37	9	1	-5	16.44	16.40	8	1	-6	10.06	8.75
7	0	4	10.22	9.18	0	-2	-5	16.98	16.30	9	1	-6	4.35	3.34
8	0	-4	24.03	23.63	1	-2	-5	42.40	40.16	0	2	6	42.11	43.31
9	0	-4	5.16	7.87	1	2	5	29.92	28.83	1	-2	-6	54.25	59.69
0	-1	-4	8.64	7.67	2	-2	-5	37.29	38.53	1	-2	6	22.28	23.74
1	-1	-4	63.12	67.26	2	2	5	5.82	5.92	2	-2	-6	35.33	34.85
1	1	4	11.25	12.36	3	-2	-5	10.32	11.59	2	2	6	12.21	13.04
2	1	-4	5.73	5.87	3	2	5	5.81	5.19	3	-2	-6	39.74	35.87
2	-1	4	7.72	10.74	4	-2	-5	12.42	8.86	3	2	6	15.38	13.96
3	-1	-4	12.39	12.12	4	2	5	17.26	17.59	4	2	-6	45.80	46.18
3	1	4	4.97	5.94	5	2	-5	12.18	13.28	4	2	6	15.23	15.95
4	1	-4	7.43	8.46	6	-2	-5	8.10	7.44	5	-2	-6	20.86	22.19
4	1	4	11.79	12.11	6	2	5	8.74	8.01	6	2	-6	15.68	18.58
5	1	4	13.86	14.19	7	2	-5	9.74	9.10	7	2	-6	22.20	21.53
6	1	-4	19.46	17.28	9	2	-5	4.77	5.01	8	2	-6	13.92	12.19
7	-1	-4	9.47	8.86	0	-3	-5	50.05	50.02	0	3	6	15.28	13.96
8	1	-4	11.88	11.13	1	-3	-5	45.44	48.17	1	-3	-6	13.61	12.21
0	-2	-4	72.69	74.86	1	3	5	36.54	36.11	1	3	6	34.84	34.83
1	-2	-4	76.68	77.35	2	-3	-5	34.94	40.05	2	-3	-6	35.46	42.36
1	2	4	41.40	43.49	2	3	5	33.29	34.26	3	3	-6	26.48	26.99
2	-2	-4	7.23	4.34	3	-3	-5	17.56	15.94	3	3	6	10.53	9.54
2	2	4	65.49	66.55	3	3	5	20.29	20.42	4	3	-6	22.50	25.48
3	-2	-4	5.18	6.09	4	3	-5	21.86	23.44	4	3	6	5.39	4.02
3	2	4	43.97	42.07	4	3	5	9.73	9.90	5	-3	-6	33.65	36.52
4	2	-4	11.35	10.46	5	3	-5	24.29	24.89	6	3	-6	6.13	6.66
4	2	4	31.53	32.34	5	3	5	7.16	8.44	0	-4	-6	28.62	29.85
5	2	-4	20.48	22.87	6	3	-5	11.17	9.64	1	-4	-6	9.41	7.09
6	2	-4	14.60	15.87	7	3	-5	10.75	12.02	1	4	6	15.31	17.26
8	2	4	4.28	3.66	8	3	-5	13.90	13.70	2	-4	-6	26.70	26.57
7	-2	-4	32.90	31.51	9	3	-5	9.69	9.09	2	4	6	18.00	18.96
7	2	4	7.63	7.24	0	4	5	20.63	20.74	3	-4	-6	40.89	44.42
8	2	-4	13.57	15.43	1	-4	-5	28.92	33.82	3	4	6	14.96	16.29
9	2	-4	7.67	5.75	1	4	5	32.46	34.20	4	4	-6	29.54	31.90
0	-3	-4	45.34	46.17	2	-4	-5	27.86	29.07	4	4	6	15.36	14.81
1	-3	-4	34.01	29.71	3	4	-5	6.60	3.76	5	4	-6	25.22	24.90

5	4	6	9.46	10.01	1	7	7	24.97	23.84								
6	4	-6	21.38	21.06	2	-7	-7	32.09	32.20								
7	4	-6	12.36	13.91	2	7	7	26.32	26.18	4	1	9	15.66	15.36			
8	4	-6	7.69	8.52	3	-7	-7	4.18	5.61	7	-1	-9	23.07	21.06			
9	4	-6	9.99	9.29	3	7	7	6.43	6.69	8	-1	-9	21.27	22.01			
0	-5	-6	25.41	25.89	4	-7	-7	14.59	14.42	9	1	-9	8.42	9.04			
1	-5	-6	6.98	7.87	5	7	-7	6.66	9.89	0	-2	-9	8.69	8.86			
1	5	6	28.31	29.55	6	7	-7	15.28	16.54	1	-2	-9	18.42	19.84			
3	-5	-6	26.53	26.17	0	8	7	5.45	5.24	2	-2	-9	8.34	10.15			
3	5	6	9.89	10.49	2	-8	-7	6.62	5.93	2	2	9	5.14	3.46			
4	5	-6	13.67	14.21	0	-9	-7	11.78	11.98	4	-2	-9	11.80	10.34			
5	5	-6	26.73	28.09	1	-9	-7	15.41	14.90	6	-2	-9	21.36	21.81			
5	5	6	6.39	5.44	1	9	7	16.19	15.03	7	-2	-9	14.01	13.14			
7	5	-6	8.56	6.94	2	-9	-7	16.38	16.58	0	-3	-9	24.05	24.16			
8	5	-6	9.63	8.62	2	-10	-7	5.08	3.54	1	-3	-9	14.77	15.38			
0	-6	-6	4.91	3.93	3	-10	-7	6.60	6.48	1	3	9	25.17	26.15			
1	-6	-6	13.26	12.38	0	0	8	18.55	19.90	2	-3	-9	20.37	19.50			
1	6	6	33.18	34.17	1	0	-8	6.96	7.10	2	3	9	12.63	13.11			
2	6	-6	23.47	25.56	1	0	8	19.75	18.68	3	-3	-9	20.00	17.68			
2	6	6	27.06	26.30	2	0	-8	8.78	9.69	3	3	9	11.56	11.28			
3	6	-6	10.54	10.63	2	0	8	21.08	20.80	4	-3	-9	8.14	7.43			
3	6	6	10.57	9.46	3	0	-8	32.32	31.73	5	3	-9	4.60	4.72			
4	6	6	11.74	11.53	3	0	8	29.55	28.31	6	3	-9	12.57	13.30			
5	6	-6	18.71	19.13	4	0	-8	36.54	34.90	7	3	-9	16.15	15.05			
6	6	-6	23.96	24.82	4	0	8	21.95	22.08	8	3	-9	12.03	11.90			
7	6	-6	7.85	9.56	5	0	-8	17.31	15.08	9	3	-9	10.31	10.76			
8	6	-6	10.88	11.48	6	0	-8	25.88	25.23	0	-4	-9	8.26	8.56			
0	-7	-6	4.73	4.24	7	0	-8	41.66	41.27	1	-4	-9	27.09	26.92			
1	7	6	8.29	7.64	8	0	-8	23.01	22.89	2	-4	-9	13.89	11.80			
2	-7	-6	11.38	11.75	0	1	8	5.73	4.39	3	-4	-9	4.54	3.43			
3	7	-6	4.24	4.95	1	-1	-8	17.78	16.59	4	-4	-9	5.67	6.99			
4	7	-6	3.91	3.48	1	-1	8	9.25	8.70	6	-4	-9	21.13	21.55			
4	7	6	4.03	1.95	2	-1	-8	6.55	8.64	7	4	-9	15.33	17.04			
0	8	6	12.19	9.35	2	1	8	13.10	12.72	8	4	-9	4.14	2.39			
1	8	6	24.01	20.59	3	-1	-8	21.46	21.70	0	-5	-9	6.95	6.17			
2	-8	-6	12.43	8.97	3	1	8	4.45	3.68	1	-5	-9	14.19	13.96			
2	8	6	21.22	21.18	4	-1	-8	7.70	8.47	1	5	9	13.85	12.15			
3	-8	-6	6.28	5.94	5	-1	-8	17.52	16.98	2	-5	-9	24.98	27.34			
3	8	6	11.23	13.22	6	1	-8	9.46	9.11	2	5	9	12.28	12.37			
5	8	-6	12.37	12.45	7	-1	-8	14.03	13.92	3	-5	-9	18.51	20.65			
6	8	-6	14.42	15.75	8	1	-8	5.30	6.16	4	-5	-9	12.00	10.63			
7	8	-6	8.06	9.71	9	1	-8	7.01	7.27	5	-5	-9	21.33	21.16			
0	-9	-6	4.34	3.97	0	-2	-8	27.19	25.95	6	-5	-9	22.13	20.31			
1	-9	-6	8.03	7.26	1	2	-8	21.26	20.47	7	5	-9	7.10	6.88			
1	9	6	8.16	8.65	1	2	8	11.68	13.29	8	5	-9	4.85	4.11			
2	-9	-6	6.34	5.41	2	-2	-8	10.94	11.39	0	-6	-9	5.95	6.35			
4	9	-6	7.11	7.50	2	2	8	16.89	16.51	1	-6	-9	11.10	11.53			
5	9	-6	6.46	6.99	3	-2	-8	14.56	11.88	4	-6	-9	9.65	8.10			
6	9	-6	3.99	1.62	3	2	8	22.58	22.38	6	-6	-9	16.10	16.08			
0	10	6	5.77	3.93	4	-2	-8	34.29	32.55	7	6	-9	8.69	8.14			
1	-10	-6	9.20	7.63	4	2	8	16.24	15.81	1	-7	-9	7.70	8.30			
1	10	6	14.29	12.57	5	-2	-8	13.54	15.36	1	7	9	7.90	9.79			
2	-10	-6	10.93	10.47	6	2	-8	10.66	11.46	2	-7	-9	32.26	32.14			
3	10	-6	8.33	9.07	7	-2	-8	32.14	32.03	3	-7	-9	21.83	20.23			
0	-1	-7	42.62	42.18	8	2	-8	23.16	23.48	4	-7	-9	7.37	5.74			
1	-1	-7	7.72	9.49	9	2	-8	4.27	5.20	5	7	-9	19.30	19.72			
1	1	7	5.11	4.79	0	-3	-8	18.73	17.28	6	7	-9	20.90	22.20			
2	1	-7	15.28	14.30	1	-3	-8	25.78	26.94	1	-9	-9	4.87	6.13			
2	-1	7	14.29	13.94	2	-3	-8	18.96	19.81	2	-9	-9	13.61	14.49			
3	-1	-7	61.47	61.90	2	3	8	7.53	8.36	3	-9	-9	12.28	12.38			
3	1	7	21.89	21.17	3	-3	-8	34.87	34.32	4	-9	-9	11.18	10.61			
4	-1	-7	92.19	93.36	3	3	8	13.14	13.10	0	0	10	38.82	38.26			
4	1	7	20.22	20.04	4	3	8	6.40	5.26	1	0	-10	24.35	25.14			
5	-1	-7	33.32	30.92	6	3	-8	13.39	14.89	1	0	10	15.90	15.57			
5	1	7	6.08	7.18	7	3	-8	3.89	4.85	2	0	-10	13.32	14.95			
6	1	-7	15.82	16.10	8	3	-8	11.92	12.45	2	0	10	5.17	4.23			
7	1	-7	37.66	39.83	9	3	-8	8.50	7.11	3	0	-10	29.04	31.16			
8	-1	-7	19.80	20.29	0	-4	-8	15.26	16.14	3	0	10	12.70	13.08			
0	-2	-7	15.79	15.25	1	-4	-8	19.06	19.19	4	0	-10	18.61	18.57			
1	-2	-7	5.95	5.46	1	4	8	20.21	20.16	5	0	-10	10.17	10.34			
1	2	7	7.57	7.76	2	-4	-8	16.11	15.87	6	0	-10	4.85	3.48			
2	2	-7	15.68	17.62	2	4	8	18.14	19.73	7	0	-10	20.41	21.24			
2	2	7	8.93	9.14	3	-4	-8	22.88	23.66	8	0	-10	10.27	9.06			
3	-2	-7	25.52	25.43	3	4	8	10.53	10.18	0	-1	-10	11.59	10.40			
3	2	7	13.01	14.14	4	-4	-8	16.43	17.34	1	-1	-10	6.56	7.54			
5	-2	-7	4.25	3.36	4	4	8	7.84	7.90	1	1	10	5.03	4.20			
6	2	-7	3.53	1.83	5	-4	-8	18.54	17.83	2	-1	-10	11.63	11.56			
8	-2	-7	14.24	14.69	6	-4	-8	19.06	17.82	5	-1	-10	15.84	15.57			
9	-2	-7	6.47	6.54	7	4	-8	13.68	13.65	7	-1	-10	12.57	12.00			
0	-3	-7	25.03	26.14	8	-4	-8	10.08	9.75	0	-2	-10	27.60	27.92			
1	-3	-7	23.33	21.95	0	-5	-8	7.47	7.11	1	-2	-10	26.96	26.89			
1	3	7	12.01	12.16	1	-5	-8	20.94	19.98	1	2	10	10.71	11.15			
2	-3	-7	15.71	12.96	1	5	8	3.98	3.71	2	-2	-10	17.92	17.63			
2	3	7	7.72	8.18	2	5	8	13.79	13.48	2	2	10	5.71	6.78			
3	3	-7	35.73	38.54	3	-5	-8	25.32	27.67	3	-2	-10	24.56	24.76			
3	3	7	13.27	13.72	3	5	8	9.05	8.69	3	2	10	10.13	9.94			
4	-3	-7	38.12	38.51	4	-5	-8	6.28	6.46	4	-2	-10	20.33	21.37			
4	3	7	14.12	14.02	5	5	8	6.91	7.11	7	2	-10	15.99	13.64			
5	3	-7	22.43	24.98	6	5	-8	17.99	16.66	8	2	-10	8.91	9.52			
5	3	7	8.12	8.12	7	5	-8	11.52	11.43	1	-3	-10	13.47	13.60			
6	3	-7	23.62	24.66	8	5	-8	9.63	8.59	1	3	10	13.74	14.94			
7	3	-7	25.09	25.05	0	6	8	11.72	11.94	2	-3	-10	8.18	7.97			
8	3	-7	14.35	13.05	1	-6	-8	22.12	23.73	4	-3	-10	13.19	13.53			
9	3	-7	5.31	4.87	1	6	8	17.69	18.87	5	-3	-10	8.32	9.45			
0	-4	-7	10.92	12.31	2	-6	-8	38.62	36.19	6	3	-10	8.66	8.56			
1	4	7	12.94	13.48	2	6	8	13.02	13.42	7	3	-10	7.79	8.85			
2	-4	-7	28.27	26.99	3	-6	-8	14.49	15.96	0	-4	-10	13.86	14.11			
2	4	7	19.03	19.12	4	-6	-8	10.83	10.45	1	-4	-10	11.66	12.52			
3	-4	-7	38.06	38.74	5	6	-8	15.06	15.71	1	4	10	11.89	11.68			
3	4	7	17.65	18.88	6	6	-8	10.46	10.31	2	-4	-10	15.82	16.20			
4	-4	-7	4.96	5.63	0	7	8	6.95	6.63	2	4	10	8.65	7.44			
5	4	-7	14.95	15.81	1	-7	-8	8.13	6.82	3	-4	-10	17.99	19.40			
6	4	-7	17.61	17.83	2	-7	-8	5.39	5.92	4	-4	-10	13.70	13.39			
9	4	-7	7.15	7.73	3	-7	-8	3.78	3.18	5	-4	-10	13.18	13.03			
0	-5	-7	19.47	19.02	5	-7	-8	9.69	9.26	6	-4	-10	20.70	19.19			
1	-5	-7	20.70	21.95	6	7	-8	7.45	7.54	7	-4	-10	11.39	12.37			
1	5	7	17.65	17.28	0	8	8	8.36	10.91	8	4	-10	5.76	6.32			
2	-5	-7	25.14	28.23	1	-8	-8	19.62	21.61	0	-5	-10	9.96	9.67			
2	5	7	20.12	20.08	1	8	8	9.20	10.37	1	-5	-10	9.07	9.38			
3	-5	-7	18.54	18.51	2	-8	-8	21.85	23.28	1	5	10	10.66	10.16			
3	5	7	17.22	17.61	2	8	8	9.49	10.29	2	-5	-10	8.65	9.40			
4	-5	-7	14.20	14.92	3	-8	-8	13.38	13.36	4	-5	-10	8.29	7.93			
4	5	7	7.95	6.78	4	-8	-8	8.73	8.75	5	-5	-10	15.20	16.58			
5	-5	-7	13.78	13.11	5	-8	-8	15.30	14.52	7	5	-10	10.50	11.01			
6	-5	-7	15.71	17.09	6	8	-8	7.51	5.92	0	-6	-10	3.82	2.17			
7	5	-7	11.48	11.69	7	-9	-8	6.51	7.45	1	6	10	7.99	7.31			
8	5	-7	5.98	5.52	5	9	-8	4.43	4.45	2	-6	-10	12.07	13.09			
0	-6	-7	6.90	6.66	2	-10	-8	15.76	16.78	3	-6	-10	13.70	12.86			
2	-6	-7	10.78	12.77	3	-10	-8	9.23	9.94	4	-6	-10	10.84	11.21			
3	-6	-7	13.34	14.24	0	-1	-9	41.89	41.60	5	6	-10	20.23	21.01			
3	6	7	9.24	8.98	1	-1	-9	22.37	20.79	6	6	-10	19.47	20.49			
4	-6	-7	3.93	4.04	1	1	9	29.36	29.10	7	-6	-10	7.67	7.58			
4	6	7	4.68	4.23	2	1	9	19.19	18.04	1	-7	-10	4.02	2.55			
5	6	-7	10.38	9.00	3	-1	-9	8.78	9.05	4	-7	-10	5.08	4.41			
0	7	7	11.45	11.07	3	1	9	21.66	21.63	1	-8	-10	4.46	3.22			
1	-7	-7	24.54	25.43	4	1	-9	16.36	15.23	2	-8	-10	9.21	8.03			

3	-8	-10	4.78	4.48
4	-8	-10	6.20	6.40
5	-8	-10	16.65	17.37
0	-1	-11	19.00	17.79
1	-1	-11	28.10	27.67
2	-1	-11	14.52	14.50
3	-1	-11	24.86	24.67
4	-1	-11	41.38	42.73
5	-1	-11	23.39	23.93
6	1	-11	7.04	6.17
7	1	-11	13.29	13.01
8	1	-11	5.37	8.70
0	-2	-11	11.45	10.39
1	2	11	10.45	11.04
2	-2	-11	5.82	7.17
3	-2	-11	7.90	8.25
4	-2	-11	9.70	8.81
5	-2	-11	13.46	13.58
6	2	-11	7.91	8.35
0	-3	-11	11.69	12.42
1	-3	-11	16.96	16.90
2	-3	-11	13.92	14.70
3	-3	-11	21.40	20.51
4	-3	-11	26.20	25.56
5	-3	-11	17.18	16.87
6	3	-11	11.49	10.46
7	3	-11	11.29	12.52
8	3	-11	5.46	7.29
0	-4	-11	12.48	12.32
1	-4	-11	5.00	4.27
1	4	11	12.26	10.90
2	-4	-11	8.01	6.54
3	-4	-11	7.50	9.19
4	-4	-11	6.51	7.01
5	-4	-11	12.54	13.55
6	-4	-11	3.91	3.57
0	5	11	3.60	2.74
1	-5	-11	9.55	9.68
2	-5	-11	12.76	12.99
3	-5	-11	5.96	7.01
4	-5	-11	6.30	6.88
5	-5	-11	13.41	13.75
6	-5	-11	15.18	15.18
7	-5	-11	10.03	9.29
0	-6	-11	7.46	6.16
2	-6	-11	9.08	8.01
3	-6	-11	5.86	5.16
4	-6	-11	6.53	5.49
5	6	-11	7.42	7.38
1	-7	-11	4.18	2.46
2	-7	-11	9.65	9.74
3	-7	-11	4.15	4.12
5	-7	-11	6.59	7.34
0	0	12	10.37	10.16
1	0	-12	8.15	8.14
2	0	-12	4.76	2.85
3	0	-12	19.51	19.79
4	0	-12	33.83	33.06
5	0	-12	21.39	20.21
6	0	-12	13.19	11.70
7	0	-12	20.52	20.52
8	0	-12	14.37	14.33
0	-1	-12	4.46	4.35
3	-1	-12	9.71	9.80
4	-1	-12	5.04	5.28
5	-1	-12	7.10	7.05
8	1	-12	4.42	3.59
0	2	12	6.64	6.24
1	-2	-12	8.26	8.07
2	-2	-12	7.65	7.55
3	-2	-12	17.27	15.07
4	2	-12	26.81	26.02
5	-2	-12	20.01	20.04
6	-2	-12	11.37	11.29
7	-2	-12	13.98	14.04
0	-3	-12	5.74	5.48
2	-3	-12	6.62	8.20
3	-3	-12	16.36	17.01
5	-3	-12	5.85	5.90
7	3	-12	4.54	3.06
0	-4	-12	6.65	6.93
1	-4	-12	8.69	8.53
2	-4	-12	12.02	12.03
3	-4	-12	10.20	9.31
4	-4	-12	8.04	7.62
5	-4	-12	11.94	12.11
6	-4	-12	12.24	11.56
7	-4	-12	8.33	7.65
3	-5	-12	16.87	17.03
4	-5	-12	5.81	6.17
5	-5	-12	6.42	6.90
2	-6	-12	13.05	13.22
5	-6	-12	6.90	7.29
2	-1	-13	7.60	6.72
4	-1	-13	13.38	12.83
5	1	-13	7.47	6.38
6	1	-13	7.57	7.15
7	1	-13	17.58	17.28
1	-2	-13	8.53	8.47
3	-2	-13	11.49	11.08
6	2	-13	6.04	7.63
3	-3	-13	7.50	7.84
4	-3	-13	10.57	9.75
5	-3	-13	5.89	5.54
6	-3	-13	7.63	7.53
3	-4	-13	9.64	10.35
4	-4	-13	5.49	4.89
4	0	-14	9.14	10.49

APPENDIX 2

Structure Factor Tables for $Cu(I)(DTO)_2BF_4$

H	K	L	Y(OBS)	Y(CALC)	A	B							
							1	6	3	53.24	50.16	46.05	-19.90
0	0	2	61.30	64.40	-32.63	-37.11	1	6	4	41.19	45.04	-44.98	-2.29
0	0	4	109.28	107.29	107.27	2.04	1	6	5	14.81	13.19	-9.57	-9.07
0	0	6	90.74	88.72	-86.26	59.00	1	6	8	18.17	23.77	-42.85	6.56
0	0	8	12.56	16.82	13.59	9.91	1	6	10	15.76	13.33	11.89	6.04
0	0	10	21.98	21.23	-17.64	-11.82	1	7	0	25.11	27.80	27.80	0.00
0	1	1	83.98	87.78	-86.11	-17.03	1	7	1	48.00	44.53	-40.72	-18.01
0	1	3	75.01	78.25	-77.47	10.99	1	7	3	24.49	26.30	23.84	-11.11
0	1	5	32.22	29.33	-29.06	3.86	1	7	4	16.05	13.62	9.63	-9.63
0	1	7	16.88	16.82	16.05	-5.03	1	7	5	11.63	10.61	-6.79	8.16
0	2	0	150.43	156.29	156.29	0.00	1	7	8	10.83	5.76	-0.13	5.76
0	2	2	37.54	37.00	-14.61	-33.99	1	8	0	40.60	40.07	-40.07	-0.00
0	2	4	69.25	74.70	39.75	44.84	1	8	1	18.15	19.56	3.27	19.28
0	2	6	26.83	28.34	-28.28	-1.76	1	8	2	59.80	64.29	60.23	22.47
0	2	8	32.00	33.01	31.44	10.09	1	8	3	24.03	22.60	22.60	0.50
0	2	10	19.83	21.72	-17.45	-12.93	1	8	4	31.83	31.39	-31.22	3.23
0	3	1	63.90	65.79	-26.30	34.03	1	8	6	11.72	11.50	7.29	8.89
0	3	3	39.00	38.90	-23.46	31.03	1	8	7	10.78	9.59	2.74	9.18
0	3	5	48.85	50.29	-49.53	-8.69	1	8	8	23.56	22.43	-22.29	-2.51
0	3	7	36.22	36.97	36.90	-2.15	1	8	10	12.52	10.52	10.20	2.59
0	3	9	18.46	17.07	0.19	-17.07	1	8	12	11.63	7.17	-1.54	-7.00
0	3	11	12.68	14.61	14.36	-2.57	1	9	0	38.94	38.05	38.05	0.00
0	4	0	115.73	117.58	-117.58	-0.00	1	9	1	22.73	20.81	-19.85	6.26
0	4	2	125.63	125.01	-113.15	-53.15	1	9	3	22.33	23.02	-22.84	-2.85
0	4	4	50.88	51.77	21.51	47.09	1	9	5	12.98	14.45	-13.09	6.12
0	4	6	40.14	36.01	6.58	-35.40	1	9	8	9.42	6.13	-3.39	5.11
0	4	8	46.72	46.42	46.19	-4.62	1	9	9	14.28	11.86	9.83	-6.64
0	4	10	15.63	19.21	-18.12	-6.37	1	10	0	42.71	43.85	-43.85	-0.00
0	5	1	111.42	108.64	-106.02	23.71	1	10	2	29.19	30.03	6.94	29.21
0	5	3	92.33	96.04	89.16	35.64	1	10	3	10.48	9.58	-6.09	7.40
0	5	7	20.24	22.00	17.00	-13.95	1	10	4	15.16	15.23	-10.09	-11.41
0	5	9	18.11	21.45	-21.43	0.88	1	10	5	9.83	9.26	-9.10	1.74
0	5	11	12.13	13.24	7.76	10.72	1	10	6	19.08	20.40	19.38	6.36
0	6	0	32.13	31.66	-31.66	-0.00	1	10	7	13.16	13.03	8.77	9.63
0	6	2	45.32	41.49	-35.50	-21.47	1	10	8	16.65	14.85	-12.13	-8.57
0	6	4	13.47	13.78	13.48	2.87	1	11	0	10.62	4.34	-4.34	0.00
0	6	6	18.19	19.98	1.16	-19.95	1	11	1	23.35	24.18	17.32	16.87
0	6	8	20.07	21.87	20.44	7.77	1	11	2	12.62	8.99	8.91	1.15
0	6	12	14.09	6.13	0.58	6.10	1	11	3	16.79	17.10	-15.18	7.87
0	7	1	61.72	60.69	-60.22	-7.52	1	11	4	11.39	10.47	-2.23	10.23
0	7	3	71.28	68.35	66.93	13.88	1	11	7	10.73	4.87	-4.66	1.43
0	7	9	25.71	26.64	-26.49	2.62	1	12	0	31.51	30.36	-30.36	-0.00
0	7	11	12.10	11.95	1.48	11.85	1	12	6	11.83	13.37	13.23	-1.95
0	8	0	82.20	83.69	83.69	0.00	1	13	1	22.09	20.47	19.88	4.85
0	8	2	16.05	13.24	-12.26	-4.99	1	14	0	13.68	10.75	-10.75	-0.00
0	8	4	15.23	17.28	10.75	-13.53	1	14	2	11.35	13.41	11.99	-6.01
0	8	6	17.58	17.46	-7.70	15.67	1	14	3	10.40	6.40	5.39	-3.46
0	9	1	54.23	54.87	-40.53	-36.98	1	14	4	11.38	6.36	-5.41	-3.35
0	9	3	25.30	29.31	18.40	22.82	1	15	1	10.27	6.94	6.64	-2.03
0	9	7	14.65	17.90	15.71	8.58	1	15	3	10.02	6.01	0.31	-6.00
0	9	9	16.82	18.09	-17.94	-2.29	1	16	1	10.60	1.30	0.70	1.10
0	10	0	20.95	23.74	23.74	0.00	2	0	0	187.22	181.52	-181.52	-0.00
0	10	2	28.70	28.76	26.95	10.05	2	0	1	65.32	69.63	-91.84	32.00
0	10	6	12.31	8.97	-7.83	4.36	2	0	2	21.22	22.73	13.55	18.25
0	11	1	27.34	28.42	-23.30	-16.28	2	0	3	46.15	47.91	-18.26	44.29
0	11	3	19.69	14.95	-5.87	13.75	2	0	4	63.08	56.43	-49.76	-30.63
0	11	5	19.15	19.33	-18.43	-5.83	2	0	5	64.22	67.94	-63.37	24.50
0	11	7	18.47	16.33	15.56	4.96	2	0	6	33.87	31.51	31.25	-6.03
0	11	9	11.35	7.38	-2.95	-6.77	2	0	7	29.72	30.24	24.37	17.90
0	12	0	24.26	27.13	-27.13	-0.00	2	0	8	15.51	14.94	-14.88	-1.28
0	12	2	18.22	20.28	19.26	6.33	2	0	9	22.38	26.59	16.72	-20.68
0	12	4	12.54	13.51	-2.17	13.33	2	0	10	21.73	21.28	15.81	14.25
0	13	1	23.83	23.83	-22.31	8.39	2	1	0	42.07	38.80	38.80	0.00
0	14	0	21.39	22.08	-22.08	-0.00	2	1	1	36.55	34.18	34.13	-1.74
0	15	1	12.99	8.93	-4.69	7.60	2	1	2	114.00	112.36	-70.68	87.34
1	1	0	122.78	119.16	119.16	0.00	2	1	3	24.42	27.71	-27.58	-2.87
1	1	1	148.87	152.84	-151.21	-22.26	2	1	4	41.19	46.33	40.37	-22.74
1	1	2	92.89	91.15	-91.41	67.36	2	1	5	29.71	28.53	23.50	16.17
1	1	3	52.29	50.70	20.48	46.38	2	1	6	37.26	38.44	36.27	12.72
1	1	4	52.79	52.73	50.33	-15.73	2	1	7	11.86	12.45	-11.97	3.41
1	1	5	66.15	70.43	-70.17	6.06	2	1	8	10.88	15.03	2.12	-15.69
1	1	6	38.19	35.01	-32.84	12.13	2	2	0	145.21	145.65	-145.65	-0.00
1	1	7	35.87	33.72	33.63	2.45	2	2	1	99.57	99.15	-48.29	95.03
1	1	8	20.46	19.05	-1.12	19.01	2	2	2	87.00	82.63	79.39	22.92
1	1	9	18.96	20.21	-13.09	-15.40	2	2	3	50.96	52.84	30.03	-17.00
1	1	10	12.03	5.08	5.06	0.46	2	2	4	60.11	61.65	-58.13	-20.53
1	1	11	12.29	18.31	15.94	9.01	2	2	5	68.73	65.73	-58.56	-4.42
1	1	12	9.82	5.30	5.09	-1.50	2	2	6	39.45	44.54	43.30	10.42
1	2	0	60.43	63.07	-63.07	-0.00	2	2	7	26.33	23.93	15.35	18.36
1	2	1	15.83	18.19	-10.10	-15.12	2	2	8	23.63	23.69	-22.69	-6.80
1	2	2	111.64	109.55	-71.98	82.58	2	2	9	13.89	11.44	-0.98	-11.40
1	2	3	40.39	39.54	-37.69	-11.95	2	2	10	15.49	17.15	14.02	9.87
1	2	4	57.54	58.30	13.48	-56.72	2	3	0	17.47	17.43	17.43	0.00
1	2	5	16.99	12.52	-12.50	-0.69	2	3	1	32.65	29.21	29.04	-3.13
1	2	6	32.88	36.08	35.52	6.35	2	3	2	51.06	49.61	-49.42	-8.33
1	2	7	15.69	15.06	13.89	5.81	2	3	3	18.29	19.79	-13.52	-13.04
1	2	8	14.77	13.23	-10.43	-8.13	2	3	4	7.50	5.49	-4.65	-2.92
1	2	9	11.37	11.63	9.17	-7.15	2	3	5	42.38	44.46	38.77	21.76
1	2	10	10.75	9.99	6.94	7.29	2	3	6	61.57	62.03	60.79	12.36
1	2	12	9.66	10.18	-8.98	4.78	2	3	7	23.10	23.81	-23.63	2.87
1	3	0	83.88	78.81	-78.81	0.00	2	3	8	21.79	22.31	6.31	-21.40
1	3	1	93.66	92.83	-91.66	14.68	2	3	9	10.14	9.96	4.39	8.94
1	3	2	41.02	40.32	38.37	-12.37	2	3	11	9.65	11.09	-10.74	-2.74
1	3	3	96.96	95.76	88.35	67.07	2	4	0	9.82	8.21	8.21	0.00
1	3	4	24.45	25.67	25.67	0.05	2	4	1	49.91	48.21	46.87	11.32
1	3	5	30.16	28.77	-22.56	-17.86	2	4	2	93.39	94.30	89.21	30.59
1	3	6	25.90	25.65	-2.58	-25.52	2	4	3	57.95	55.24	35.03	4.81
1	3	7	28.73	29.49	27.42	10.66	2	4	4	27.03	27.82	-25.64	-10.81
1	3	8	11.35	9.54	8.56	4.21	2	4	5	46.37	44.56	-15.17	-41.90
1	3	9	31.80	31.00	-30.79	-3.64	2	4	6	31.80	29.86	21.36	20.87
1	3	10	9.24	3.24	-3.01	-1.21	2	4	7	25.24	22.17	2.40	22.04
1	3	11	13.23	14.40	8.75	11.43	2	4	8	26.67	27.66	-25.26	-11.28
1	4	0	119.28	117.87	-117.87	-0.00	2	4	9	20.31	23.29	-22.28	6.79
1	4	1	35.21	37.86	-17.94	-33.34	2	4	10	13.16	10.15	9.32	4.02
1	4	2	39.43	36.60	31.21	19.11	2	5	0	33.75	36.03	-36.03	-0.00
1	4	3	29.24	31.34	11.70	-29.07	2	5	1	67.19	67.35	67.24	-3.76
1	4	4	40.22	37.11	-18.90	-31.93	2	5	2	49.92	52.16	30.35	-42.42
1	4	5	22.98	26.03	-25.98	1.48	2	5	3	50.36	50.00	-47.39	-15.94
1	4	6	26.67	27.56	27.03	-5.37	2	5	4	50.78	50.39	-50.23	-3.96
1	4	7	5.83	12.98	9.60	8.73	2	5	5	19.84	19.69	19.34	-3.72
1	4	8	14.39	14.97	-14.79	-2.27	2	5	6	9.18	9.94	5.65	8.18
1	4	10	17.18	13.57	10.48	8.63	2	5	7	19.18	19.36	-19.18	-2.60
1	5	0	38.59	40.34	-40.34	0.00	2	5	9	13.56	11.57	11.21	2.86
1	5	1	23.39	25.79	-20.71	-15.36	2	6	1	8.75	9.43	3.81	-8.63
1	5	3	89.87	92.86	84.08	39.41	2	6	2	46.22	47.10	46.11	9.63
1	5	4	31.74	30.70	25.43	17.20	2	6	3	52.86	54.65	48.91	-24.39
1	5	5	18.76	18.25	7.97	-16.42	2	6	4	16.85	16.22	-16.09	2.05
1	5	6	23.30	24.84	10.18	-22.66	2	6	5	12.83	12.53	-10.19	7.29
1	5	7	21.48	21.56	18.70	10.74	2	6	6	12.27	12.09	7.40	9.56
1	5	8	13.86	12.52	11.96	-3.72	2	6	7	20.43	21.47	9.85	19.08
1	5	9	29.91	28.24	-28.07	3.15	2	6	8	15.94	14.44	-12.76	-6.75
1	6	0	57.13	59.59	-59.59	-0.00	2	6	10	8.80	3.97	3.52	1.84
1	6	1	31.46	31.13	-1.81	31.07	2	7	1	44.83	44.70	43.38	10.78
1	6	2	107.00	107.68	107.67	-1.39	2	7	2	60.89	64.39	52.01	-37.96

2	7	3	50.78	51.01	-50.50	-7.19	3	10	4	24.30	23.38	22.62	5.90
2	7	4	60.51	62.45	-58.61	21.57	3	10	5	19.96	19.55	18.86	5.14
2	7	5	11.71	11.93	10.68	-5.31	3	10	7	25.56	23.66	-18.04	-15.31
2	7	6	11.81	11.06	-1.27	10.99	3	11	2	15.11	15.29	-15.27	-0.60
2	7	7	16.18	16.62	-13.88	-9.15	3	11	3	9.94	8.45	8.42	-0.62
2	7	9	14.55	15.87	15.86	0.65	3	11	4	15.33	17.11	5.72	-16.13
2	8	0	29.82	28.09	-28.09	-0.00	3	12	0	13.41	11.50	11.50	-0.00
2	8	1	38.75	37.02	-36.97	1.87	3	12	1	12.40	11.30	10.95	-2.77
2	8	3	8.93	8.71	-7.42	4.55	3	12	4	12.76	11.37	8.98	6.97
2	8	5	20.14	21.54	-0.99	21.52	3	12	5	16.80	16.80	16.36	3.65
2	9	0	11.23	12.36	12.36	0.00	3	12	7	11.32	6.38	-5.64	-2.26
2	9	1	36.61	36.23	30.78	19.11	3	13	0	14.25	15.02	15.02	0.00
2	9	2	11.50	10.76	8.79	6.20	3	14	1	13.44	13.50	8.88	-5.64
2	9	3	20.57	24.25	-23.32	-6.65	3	15	6	13.89	5.87	-5.52	-2.00
2	9	4	15.58	15.05	-14.38	-4.42	3	16	4	9.90	1.18	-0.14	-1.17
2	9	5	13.39	17.16	17.16	8.52	4	0	0	140.45	145.68	-145.68	-0.00
2	9	6	19.12	13.34	10.59	11.10	4	0	1	99.94	103.20	95.82	-38.35
2	9	7	10.97	15.03	-12.93	-7.65	4	0	2	85.96	90.03	-78.35	44.36
2	9	8	15.68	16.54	-10.97	-12.38	4	0	3	71.44	64.02	-57.06	16.32
2	9	9	12.18	12.07	11.64	3.19	4	0	4	82.14	80.86	68.66	42.74
2	10	1	12.99	12.79	-8.82	9.26	4	0	5	59.47	59.82	34.28	25.15
2	10	2	13.94	14.61	-12.59	-7.41	4	0	6	49.27	51.09	-24.82	-44.65
2	10	3	19.39	22.65	-20.75	9.07	4	0	7	25.83	27.63	-26.47	7.94
2	10	4	5.72	5.46	1.89	-7.52	4	0	8	25.71	21.80	21.77	1.19
2	10	5	11.44	7.05	-6.16	3.40	4	0	9	23.84	21.94	-2.77	21.76
2	11	0	11.15	9.33	-9.33	-0.00	4	1	0	12.24	11.43	-11.43	0.00
2	11	1	22.72	21.74	21.46	3.48	4	1	1	65.08	64.99	25.61	33.53
2	11	3	11.46	11.11	-9.73	-5.36	4	1	2	16.43	15.33	-1.63	15.24
2	11	5	19.87	18.43	15.84	9.42	4	1	3	53.13	46.24	34.16	-31.16
2	11	6	19.48	19.97	19.34	5.00	4	1	4	37.77	38.47	1.31	38.45
2	11	7	11.37	9.32	-9.26	-1.02	4	1	6	26.74	24.32	-24.09	-3.38
2	12	0	11.40	12.56	12.56	0.00	4	1	7	9.03	9.70	-8.58	-4.53
2	12	1	13.39	13.29	12.85	3.38	4	1	8	9.58	6.11	-1.18	5.99
2	12	3	17.16	14.61	-7.14	12.74	4	2	0	12.90	14.49	14.49	-0.00
2	12	5	12.91	12.69	6.14	-11.09	4	2	1	51.63	47.79	47.69	3.05
2	12	8	11.30	2.78	2.77	0.12	4	2	2	55.62	60.91	-58.83	15.78
2	13	0	14.46	14.74	-14.74	-0.00	4	2	3	54.89	53.10	-48.22	22.24
2	13	1	10.06	13.07	12.08	-5.00	4	2	4	43.96	40.72	40.66	-2.25
2	14	0	10.55	12.46	12.46	0.00	4	2	5	60.86	59.29	56.24	18.77
2	14	4	9.95	6.04	4.14	4.40	4	2	6	30.29	30.56	-28.50	-11.03
2	15	2	12.25	8.91	8.04	-8.56	4	2	7	33.86	29.81	-25.68	-15.14
3	1	0	107.99	100.85	-100.85	-0.00	4	2	9	15.53	16.39	7.23	14.71
3	1	1	63.97	60.04	49.36	-34.18	4	3	0	26.67	25.32	25.32	0.00
3	1	2	105.11	103.91	34.18	-98.12	4	3	1	43.03	45.11	-37.29	30.40
3	1	3	61.66	60.03	-55.88	21.94	4	3	2	25.59	23.14	-12.40	21.87
3	1	4	69.33	63.33	-53.23	-3.64	4	3	3	70.95	74.42	67.16	-32.02
3	1	5	64.20	63.90	49.17	40.81	4	3	4	33.85	30.63	21.57	21.75
3	1	6	66.55	64.96	53.37	-14.31	4	3	5	17.68	22.45	-20.12	-3.60
3	1	7	24.47	22.58	-22.46	-2.35	4	3	6	51.38	49.55	-48.77	-8.76
3	1	8	31.70	30.39	4.86	-30.00	4	3	7	9.83	10.62	-4.96	-9.39
3	1	9	14.48	16.09	11.05	11.69	4	3	8	13.83	12.84	-1.80	12.71
3	2	0	152.31	149.08	149.08	0.00	4	4	0	49.37	52.79	52.79	0.00
3	2	1	58.46	54.50	49.77	22.22	4	4	1	30.50	29.63	11.93	27.13
3	2	2	50.19	52.56	5.11	50.10	4	4	2	12.40	12.47	-8.17	9.42
3	2	3	53.10	51.07	45.25	-23.68	4	4	3	62.46	59.76	-59.71	-2.28
3	2	4	60.24	53.63	44.37	30.14	4	4	4	38.81	39.50	16.42	-35.92
3	2	5	55.90	55.96	52.46	19.46	4	4	5	39.99	40.51	35.50	19.53
3	2	6	9.70	7.46	-6.29	6.10	4	4	6	39.52	39.40	-39.35	-2.01
3	2	7	26.98	30.13	-28.77	-8.97	4	4	7	38.30	36.52	-21.79	-29.31
3	2	9	16.44	17.48	-7.45	13.81	4	4	8	22.33	22.47	-7.86	21.05
3	2	10	12.93	13.78	-8.63	-6.44	4	4	9	21.07	19.53	19.51	0.98
3	2	11	13.09	14.57	-12.57	7.37	4	5	0	35.27	34.78	34.78	-0.00
3	3	0	31.82	32.78	32.78	-0.00	4	5	1	14.84	9.17	7.31	-3.64
3	3	1	51.80	49.50	45.49	19.53	4	5	2	41.86	41.84	-40.87	8.48
3	3	2	41.05	42.43	42.12	5.14	4	5	4	35.76	38.22	35.73	-13.59
3	3	3	53.86	56.22	-56.16	1.99	4	5	5	36.41	38.88	-38.42	-6.01
3	3	4	65.34	68.64	-67.67	-11.49	4	5	6	24.53	24.74	-22.56	-10.11
3	3	5	28.14	29.11	29.01	2.37	4	5	7	27.90	29.58	17.22	24.05
3	3	6	51.19	51.44	45.33	44.77	4	5	9	12.33	7.82	-0.50	-7.81
3	3	7	25.54	29.32	-25.56	-14.36	4	6	0	17.93	14.23	14.23	-0.00
3	3	8	26.99	24.56	-22.84	-9.02	4	6	1	11.99	10.72	8.75	6.20
3	3	11	9.46	4.05	-3.89	-1.11	4	6	2	14.42	17.76	-16.89	-8.06
3	4	0	39.51	36.94	36.94	-0.00	4	6	3	44.43	48.65	-48.56	2.89
3	4	1	22.51	24.50	23.66	6.30	4	6	5	9.89	10.08	10.01	1.15
3	4	2	34.97	34.37	-28.04	19.88	4	6	6	16.16	14.40	-13.87	-3.89
3	4	3	25.66	23.35	-11.17	20.51	4	6	7	21.69	23.95	-11.74	-17.35
3	4	4	39.54	40.27	38.48	17.05	4	7	0	9.95	10.51	10.51	0.00
3	4	5	47.87	52.08	48.90	17.91	4	7	1	21.89	22.46	-14.96	-18.75
3	4	6	15.88	15.82	-15.13	-4.61	4	7	2	52.89	53.85	-53.59	5.25
3	4	7	16.33	15.62	-15.24	-6.63	4	7	3	13.62	12.15	10.17	8.64
3	4	10	13.17	8.97	-7.33	-5.16	4	7	5	26.07	25.30	-25.30	-0.31
3	5	0	44.76	45.81	45.81	0.00	4	7	6	13.05	15.35	-7.54	-13.38
3	5	1	69.87	67.88	53.55	41.72	4	7	7	25.96	26.46	20.87	16.52
3	5	2	36.00	36.07	28.36	22.29	4	7	8	16.86	17.79	17.01	5.22
3	5	3	25.17	23.84	-23.43	3.16	4	8	0	31.89	35.87	-35.87	-0.00
3	5	4	41.33	41.16	-40.86	5.00	4	8	1	21.18	21.13	20.58	-4.79
3	5	5	26.96	27.51	25.97	-9.09	4	8	4	22.92	22.62	8.45	21.68
3	5	6	41.28	42.44	-5.07	42.14	4	8	9	10.37	7.46	-6.52	3.63
3	5	7	22.47	25.08	-17.63	-17.84	4	9	0	9.86	10.32	10.32	0.00
3	5	8	25.30	23.31	-23.29	-0.89	4	9	1	8.45	12.36	-7.07	10.14
3	6	0	15.21	10.62	10.62	0.00	4	9	2	25.23	23.92	-25.23	-5.96
3	6	1	41.07	37.53	27.07	-25.49	4	9	3	30.28	32.56	28.66	-15.45
3	6	2	35.01	34.38	-28.37	-19.38	4	9	4	26.71	25.79	25.70	2.21
3	6	3	93.33	91.32	-90.34	43.41	4	9	5	15.11	15.46	-14.69	-4.82
3	6	4	15.24	14.35	14.46	-12.85	4	9	6	18.43	18.31	-14.52	-11.16
3	6	5	27.60	24.18	24.16	-0.44	4	9	8	16.75	17.28	13.32	11.01
3	6	6	36.13	33.25	-32.30	-14.10	4	9	10	9.85	2.97	-2.96	-0.17
3	6	8	16.21	17.76	11.87	13.21	4	10	1	9.02	7.91	2.58	-7.45
3	6	11	13.96	7.16	3.01	-8.49	4	10	2	13.91	9.28	-8.20	1.15
3	7	0	29.29	31.39	-31.39	-0.00	4	10	3	15.94	16.61	16.17	-3.81
3	7	1	13.09	9.16	2.02	8.93	4	10	5	10.40	6.96	2.60	6.46
3	7	2	19.02	15.70	15.70	0.48	4	10	7	11.27	8.15	3.96	7.12
3	7	3	13.30	12.56	-12.14	3.22	4	11	0	14.59	14.45	14.45	0.00
3	7	4	23.79	22.52	-14.21	17.47	4	11	1	16.25	15.26	-8.32	12.79
3	7	5	15.12	16.22	4.81	15.49	4	11	2	9.08	5.45	-4.59	2.94
3	8	0	14.16	16.72	16.72	0.00	4	11	3	23.52	23.04	21.11	-9.25
3	8	1	13.37	16.16	-1.16	-16.12	4	11	4	16.36	16.19	14.63	10.50
3	8	2	39.71	35.26	-37.45	-7.83	4	11	5	9.55	9.24	-5.38	-7.52
3	8	3	47.41	47.07	-46.72	5.79	4	11	6	10.96	17.13	-16.43	-4.87
3	8	4	23.46	21.30	20.28	-6.50	4	11	9	10.81	3.06	-2.87	-1.05
3	8	5	13.68	14.90	14.80	1.74	4	12	1	11.22	9.68	-9.26	2.83
3	8	6	15.93	21.88	-19.28	-10.34	4	12	4	14.53	14.55	-10.36	-10.22
3	8	7	19.63	22.30	-11.15	-19.30	4	13	0	19.20	15.42	15.42	0.00
3	8	8	11.28	12.71	10.24	7.53	4	13	2	10.62	7.61	-4.94	5.79
3	9	0	39.14	39.70	-39.70	-0.00	4	13	6	13.31	7.19	-7.17	-0.48
3	9	1	11.92	11.27	-10.10	-4.98	4	14	5	12.76	8.17	-7.95	-1.86
3	9	2	11.31	8.31	-7.29	-3.98	4	15	5	13.52	2.65	-2.54	0.75
3	9	5	14.30	16.40	-2.16	16.26	5	1	0	72.27	74.30	74.30	0.00
3	9	6	15.46	13.41	6.64	-13.91	5	1	1	63.64	63.35	61.08	16.80
3	9	7	9.72	7.43	2.26	7.08	5	1	2	100.88	97.70	-90.43	37.00
3	10	0	11.27	11.28	11.28	0.00	5	1	3	71.89	72.22	68.93	-21.56
3	10	1	9.15	5.15	4.71	2.10	5	1	4	66.89	67.99	56.40	37.96
3	10	2	29.34	28.70	-26.51	11.01	5	1	5	43.69	44.13	-12.01	-42.47
3	10	3	13.69	14.68	-5.27	-12.13	5	1	6	55.54	54.88	-34.82	-2.62
							5	1	7	22.33	24.29	18.47	15.77

5	1	8	9.88	11.74	10.31	5.60	6	4	8	15.99	13.97	13.88	-1.53
5	1	9	10.00	8.06	-7.06	-3.89	6	5	0	53.07	51.23	-51.23	-0.00
5	2	0	11.98	16.06	16.06	-0.00	6	5	1	19.45	23.07	-42.70	-4.16
5	2	1	35.93	37.49	-30.86	21.30	6	5	2	49.34	51.89	43.74	27.91
5	2	2	66.50	65.00	30.39	-57.46	6	5	3	8.00	9.26	5.23	7.64
5	2	3	8.18	10.16	9.19	4.32	6	5	4	19.31	17.35	-17.35	-0.50
5	2	4	35.67	32.77	-30.85	11.05	6	5	5	20.57	20.45	18.76	8.14
5	2	5	36.09	35.44	-25.42	-24.70	6	5	6	32.41	30.29	29.59	6.51
5	2	6	23.13	22.27	-21.58	-5.50	6	5	7	12.23	12.19	-1.78	-12.06
5	2	7	22.77	19.84	4.40	-19.35	6	5	8	18.76	18.39	-16.24	-8.62
5	3	0	36.72	40.78	40.78	0.00	6	5	10	9.62	7.51	6.85	3.07
5	3	1	34.01	34.32	-34.00	-4.66	6	6	0	20.08	22.94	-22.94	0.00
5	3	2	66.47	65.80	-01.07	-24.49	6	6	1	29.02	28.90	-26.41	-11.73
5	3	3	37.45	36.38	9.38	-35.15	6	6	2	14.64	14.21	-13.15	-5.39
5	3	4	29.55	31.20	31.06	2.98	6	6	3	23.26	23.71	20.54	11.84
5	3	5	36.92	38.13	-34.59	16.04	6	6	7	12.14	13.13	9.55	9.02
5	3	6	33.61	34.58	-30.86	-15.61	6	7	0	49.97	50.24	-50.24	-0.00
5	3	8	21.08	20.62	17.64	10.68	6	7	1	9.30	13.55	-10.86	-8.10
5	3	9	11.99	10.23	9.20	-4.48	6	7	2	61.48	62.13	41.23	46.48
5	3	10	10.24	9.92	-7.88	-6.03	6	7	3	15.59	13.45	13.31	-1.95
5	4	0	16.57	17.18	17.18	-0.00	6	7	4	14.94	12.85	-9.62	8.52
5	4	1	54.29	58.36	-26.95	12.73	6	7	5	17.54	21.07	19.95	6.76
5	4	2	10.79	8.77	1.75	-8.59	6	7	6	19.36	23.04	21.21	8.99
5	4	3	30.29	29.99	29.31	6.32	6	7	8	15.22	20.38	-18.65	-8.22
5	4	4	23.52	24.10	-21.04	11.74	6	7	9	10.31	5.24	-3.73	3.67
5	4	5	43.22	43.44	-39.70	-17.63	6	8	0	24.05	25.18	25.18	0.00
5	4	6	17.59	18.44	8.56	16.33	6	8	1	13.74	13.05	8.48	11.33
5	4	7	11.86	14.96	12.27	-8.56	6	8	3	14.60	14.34	13.99	3.16
5	4	9	14.86	12.71	-9.49	-8.46	6	8	4	13.34	12.40	-1.38	-12.33
5	5	0	20.72	19.92	19.92	0.00	6	8	5	18.44	21.96	-3.74	-21.64
5	5	1	35.45	35.88	-32.11	16.02	6	8	6	9.61	6.40	-2.88	3.71
5	5	2	53.70	55.61	-37.40	-41.16	6	8	10	9.40	0.80	0.72	-0.37
5	5	3	24.61	23.23	13.86	-18.64	6	9	0	30.50	29.40	-29.40	-0.00
5	5	4	23.41	24.67	13.34	-20.75	6	9	1	18.00	19.86	0.35	-19.86
5	5	5	40.05	39.23	-32.15	22.48	6	9	2	32.11	33.68	33.61	2.23
5	5	6	23.30	24.48	-14.43	-19.78	6	9	3	16.08	14.18	-10.26	9.79
5	5	8	20.72	21.05	17.06	12.34	6	9	4	20.39	21.02	-21.01	0.81
5	6	1	43.64	46.04	-38.23	-25.65	6	9	8	10.34	10.18	-10.17	-0.49
5	6	2	11.65	11.66	-7.18	9.19	6	10	0	9.06	7.13	7.13	0.00
5	6	3	28.73	29.68	29.65	-1.25	6	10	1	10.77	6.76	6.28	2.49
5	6	4	15.94	14.41	-13.98	3.52	6	10	3	10.26	5.37	-5.24	-1.15
5	6	5	25.22	25.68	-45.17	5.10	6	10	5	13.24	11.37	0.96	-11.33
5	6	6	40.74	38.10	33.10	18.88	6	11	0	16.94	17.80	-17.80	-0.00
5	6	7	25.49	27.27	20.28	18.22	6	11	2	15.36	17.51	16.26	-6.50
5	6	8	16.90	15.69	-2.63	-15.47	6	11	3	14.93	13.73	-10.95	8.29
5	7	1	11.47	13.76	9.20	10.23	6	11	4	19.96	18.12	-13.48	-12.11
5	7	2	19.85	20.34	-20.04	-3.49	6	12	0	16.04	10.47	-10.47	0.00
5	7	3	7.73	11.45	-1.36	11.37	6	12	2	9.42	5.79	5.55	1.67
5	7	4	14.59	11.33	10.65	3.86	6	12	3	13.48	12.39	-9.90	-7.45
5	7	5	18.34	18.34	-8.86	-16.06	6	13	0	11.58	9.94	-9.94	-0.00
5	7	10	10.17	3.15	-2.35	-2.09	7	1	0	49.34	49.57	-49.57	-0.00
5	8	1	33.08	31.33	-25.18	-18.65	7	1	1	34.26	33.57	-31.47	11.69
5	8	2	12.62	14.73	3.89	-14.21	7	1	2	62.94	66.14	62.46	21.74
5	8	3	41.24	40.66	40.59	2.40	7	1	3	12.08	8.76	-6.49	5.89
5	8	4	9.82	12.33	-12.33	-0.41	7	1	4	41.86	49.62	-30.66	-39.01
5	8	5	15.99	12.73	-12.51	2.36	7	1	5	21.12	21.54	-15.45	-15.00
5	8	6	15.89	18.13	17.88	3.03	7	1	6	27.06	23.75	19.94	12.90
5	8	7	25.21	24.51	18.81	15.72	7	1	7	13.15	12.51	-4.29	-11.75
5	9	1	19.60	17.62	17.24	-3.64	7	1	8	24.99	25.31	-24.45	6.51
5	9	2	20.91	18.10	-0.93	18.07	7	1	10	11.63	22.78	19.03	12.53
5	9	3	13.25	12.75	11.74	4.97	7	2	1	51.71	50.11	45.50	-20.98
5	9	4	10.26	14.85	3.36	14.46	7	2	2	37.61	36.89	-35.59	-9.72
5	9	5	19.55	18.46	8.34	-16.47	7	2	3	54.40	54.25	-52.70	12.88
5	9	10	9.65	5.11	-2.31	-4.56	7	2	4	30.00	31.21	-1.11	-31.20
5	9	11	11.11	2.67	0.16	2.67	7	2	5	11.24	12.46	-1.51	12.37
5	10	1	16.58	16.28	-15.09	6.11	7	2	7	26.17	25.83	3.34	25.61
5	10	2	25.99	30.82	17.12	-25.63	7	3	0	99.39	98.06	-98.06	-0.00
5	10	3	23.90	25.25	24.94	3.94	7	3	1	20.68	20.67	-9.78	-18.21
5	10	4	17.08	17.36	-17.05	3.30	7	3	2	65.85	63.40	54.86	31.78
5	10	5	13.68	14.73	-10.84	-9.97	7	3	3	14.52	10.86	8.69	6.51
5	11	1	9.51	10.54	-6.54	-8.27	7	3	4	14.63	14.69	-13.43	5.94
5	11	2	11.47	9.14	8.84	2.31	7	3	6	21.25	24.10	22.93	-7.41
5	11	4	10.61	9.33	-8.86	2.90	7	3	7	12.80	11.75	11.62	1.74
5	11	5	10.52	10.07	8.48	5.43	7	3	8	14.10	14.27	-12.58	-6.75
5	12	0	10.85	5.63	5.63	0.00	7	4	0	13.89	14.41	-14.41	0.00
5	12	1	18.27	15.90	-14.92	5.49	7	4	1	48.63	47.56	47.18	6.01
5	12	4	10.94	7.35	-7.35	0.07	7	4	3	25.65	25.37	-19.75	-15.92
5	12	5	13.68	14.36	-12.11	-7.70	7	4	4	19.41	18.36	2.53	-18.18
5	13	0	9.86	9.82	-9.82	-0.00	7	4	5	12.81	12.25	10.60	6.14
5	13	4	11.73	9.95	-8.99	-4.26	7	4	7	13.66	13.85	-11.52	7.69
5	14	1	11.93	7.60	-7.55	-0.93	7	4	9	10.27	11.95	11.30	3.87
5	15	0	10.50	9.32	-9.32	-0.00	7	5	0	53.67	55.14	-55.14	-0.00
6	0	0	107.70	108.13	108.13	0.00	7	5	1	33.03	34.82	-0.58	-34.82
6	0	1	62.36	60.60	-00.58	1.48	7	5	2	34.80	38.43	31.64	21.80
6	0	2	15.12	15.71	-10.99	-11.22	7	5	3	12.25	11.33	11.30	-0.85
6	0	3	56.72	55.97	52.23	20.09	7	5	4	11.12	9.38	-6.61	6.66
6	0	4	19.42	15.62	-12.19	-9.77	7	5	5	13.82	12.84	11.25	6.18
6	0	5	69.89	71.40	-39.03	-59.79	7	5	6	12.29	11.93	10.39	-5.87
6	0	6	23.67	22.24	1.86	22.17	7	5	7	16.13	13.04	10.71	7.44
6	0	7	23.77	26.76	23.17	-13.38	7	6	0	22.55	21.40	-21.40	0.00
6	0	8	19.73	18.72	-12.58	-13.86	7	6	1	44.08	44.84	33.41	29.91
6	0	9	30.59	26.96	-23.32	-13.52	7	6	2	31.74	30.92	27.71	13.72
6	0	11	13.53	19.30	14.87	12.30	7	6	3	29.79	30.19	-5.27	-29.72
6	1	0	8.32	14.83	-14.83	-0.00	7	6	4	13.42	13.34	-1.55	13.25
6	1	1	17.95	15.48	15.45	0.92	7	6	5	11.32	15.62	15.62	-0.11
6	1	2	58.05	56.80	7.40	-56.32	7	6	7	26.72	26.63	-23.13	-13.20
6	1	3	37.33	34.37	-26.40	22.00	7	6	9	16.11	12.13	11.42	4.07
6	1	4	36.51	35.87	-27.00	-23.62	7	7	1	11.30	11.68	-9.78	-6.38
6	1	5	10.79	11.10	-0.75	-11.08	7	7	2	8.40	6.87	4.63	5.07
6	1	6	9.91	11.73	0.35	-11.72	7	7	3	13.32	13.14	10.32	-8.13
6	1	8	10.01	5.29	2.62	4.60	7	7	4	24.12	20.54	-10.20	-17.83
6	2	0	25.23	26.11	26.11	0.00	7	7	11	9.99	1.50	-0.90	1.20
6	2	1	88.51	84.28	-78.40	-30.93	7	8	1	36.89	40.02	34.53	20.23
6	2	2	28.78	26.81	5.10	-26.32	7	8	2	20.63	20.42	15.19	13.65
6	2	3	40.76	41.89	36.22	21.04	7	8	3	24.78	22.54	-18.21	-13.28
6	2	4	22.35	19.19	-18.11	6.33	7	8	4	10.08	9.72	0.14	9.72
6	2	5	36.66	35.47	-23.88	-26.24	7	8	7	15.13	13.84	-12.95	-4.90
6	2	6	10.18	8.46	2.73	8.01	7	9	0	16.74	15.67	15.67	0.00
6	2	7	24.06	24.08	24.01	-1.76	7	9	1	11.88	10.12	-3.07	9.65
6	2	8	9.76	5.85	-1.88	-5.54	7	9	2	13.53	11.10	-6.55	-8.96
6	2	9	21.22	19.83	-17.52	-9.29	7	9	4	13.94	15.36	-5.16	-14.46
6	3	0	28.39	28.96	-28.96	0.00	7	9	5	11.19	8.98	-5.99	-8.69
6	3	1	9.17	2.58	-1.81	-1.83	7	9	7	11.14	7.92	-4.66	-6.40
6	3	2	38.17	37.20	9.01	-36.09	7	10	1	29.03	28.83	28.64	-3.30
6	3	3	23.28	24.65	-24.06	24.93	7	10	3	21.71	22.02	-22.02	0.23
6	3	4	52.15	51.16	-14.17	-49.15	7	10	5	9.26	6.89	6.13	3.15
6	3	5	13.71	10.46	-7.08	-7.70	7	10	8	10.41	2.89	-1.53	2.45
6	3	6	12.24	9.60	1.95	-9.40	7	11	2	12.06	5.07	-0.25	-5.07
6	4	0	38.50	40.03	-40.03	0.00	7	12	1	15.36	12.82	12.33	-3.53
6	4	1	80.92	78.03	-08.91	-32.13	7	12	3	9.70	9.35	-7.86	-5.07
6	4	2	29.22	30.05	-10.12	-28.29	7	12	5	11.05	6.81	3.56	5.80
6	4	3	36.26	38.60	37.66	-8.36	7	12	6	10.11	3.68	3.12	-1.95
6	4	4	26.62	29.48	-19.22	22.36	7	13	4	13.47	10.98	5.15	9.69
6	4	5	37.98	37.03	-24.13	28.09	7	14	4	10.85	0.95	0.52	-0.79
6	4	6	17.30	13.21	12.56	-4.12	8	0	0	12.53	9.84	-9.84	-0.00
6	4	7	27.84	26.99	21.70	16.05	8	0	1	55.94	54.97	43.49	33.61

8	0	2	32.13	33.35	13.51	*30.49	9	8	1	23.35	21.22	*21.21	0.54		
8	0	3	35.25	34.79	*17.64	*29.99	9	8	2	20.58	18.21	*18.04	*2.47		
8	0	4	41.93	41.89	*32.26	*26.72	9	8	3	10.80	11.79	7.65	8.98		
8	0	5	28.92	29.16	14.70	25.18	9	8	4	19.10	16.31	13.66	*8.88		
8	0	6	23.17	20.24	14.72	13.89	9	8	6	12.16	11.78	*8.92	*7.68		
8	0	7	21.72	21.45	*21.45	0.12	9	9	2	13.28	10.64	8.14	*6.85		
8	0	8	10.55	7.95	1.14	7.87	9	9	5	10.75	12.02	1.15	11.97		
8	0	9	16.34	20.57	20.46	2.11	9	9	6	10.54	3.18	*0.20	*3.17		
8	1	0	35.24	34.04	34.04	0.00	9	10	1	22.49	21.82	*21.24	*4.97		
8	1	1	27.07	27.81	1.25	*27.78	9	10	2	19.04	19.32	*14.80	12.41		
8	1	2	24.17	20.99	*14.15	15.50	9	10	4	15.71	14.59	14.59	0.42		
8	1	4	14.06	12.56	12.43	*1.80	9	10	5	11.61	5.90	*5.37	2.43		
8	1	5	22.32	19.43	15.45	11.79	9	11	0	9.06	4.23	*4.23	*0.00		
8	1	6	10.24	7.41	1.06	7.33	9	12	2	9.84	7.36	*2.59	6.89		
8	1	7	12.85	9.99	7.61	6.47	9	12	4	12.74	8.86	5.74	6.74		
8	2	0	28.27	28.81	*28.81	*0.00	10	0	1	40.95	39.52	*21.83	*32.45		
8	2	1	57.83	58.07	55.77	16.21	10	0	2	21.99	21.72	*7.12	20.52		
8	2	2	28.11	27.92	26.94	*7.32	10	0	3	14.55	13.18	11.23	6.90		
8	2	3	35.65	38.66	*28.14	*26.50	10	0	4	40.95	41.28	35.57	20.44		
8	2	4	19.94	22.51	*20.66	*8.95	10	0	5	12.36	8.52	*6.16	5.86		
8	2	5	11.29	11.05	9.38	5.84	10	0	6	27.64	28.76	*22.72	*17.64		
8	2	6	11.77	14.76	14.69	1.45	10	0	7	19.44	20.31	15.15	13.53		
8	2	7	16.64	14.93	*14.75	2.32	10	0	8	11.78	11.55	9.59	6.44		
8	2	9	11.97	15.50	15.37	2.06	10	1	0	8.90	10.09	*10.09	*0.00		
8	3	0	47.89	51.30	51.30	0.00	10	1	1	19.42	20.44	*13.58	15.27		
8	3	1	43.50	44.46	19.34	*40.04	10	1	2	15.96	17.86	2.87	17.63		
8	3	2	39.97	38.87	*38.27	6.84	10	1	3	13.89	14.75	10.03	*10.82		
8	3	3	10.35	10.87	*10.00	*4.26	10	1	4	11.66	12.39	2.44	12.15		
8	3	4	20.37	20.56	18.15	9.65	10	1	5	9.77	11.11	*11.07	0.95		
8	3	5	26.17	25.30	22.26	12.02	10	1	6	5.61	2.79	0.78	2.68		
8	3	6	11.15	11.34	1.48	11.24	10	2	0	12.24	14.02	14.02	0.00		
8	3	7	11.99	16.21	8.06	14.06	10	2	1	19.70	19.32	*19.30	*0.75		
8	4	1	62.27	61.82	91.65	*4.66	10	2	2	22.02	23.04	*17.78	14.65		
8	4	2	17.37	20.38	11.61	16.74	10	2	3	19.16	18.53	18.30	2.96		
8	4	3	30.46	31.40	*29.16	*11.63	10	2	4	30.35	31.89	31.62	4.20		
8	4	4	18.96	17.82	0.65	17.81	10	2	5	13.77	13.03	*12.80	2.43		
8	4	5	21.94	22.23	14.80	*16.59	10	2	6	19.12	20.26	*17.40	*10.37		
8	4	6	10.60	14.85	14.14	4.52	10	2	7	11.65	11.18	9.04	6.58		
8	4	8	15.53	17.56	*5.47	*16.68	10	3	0	5.73	12.35	*12.35	*0.00		
8	5	0	18.24	20.56	20.56	0.00	10	3	1	33.04	31.31	*20.47	23.69		
8	5	1	10.83	7.96	7.42	*2.88	10	3	2	19.09	18.08	8.42	15.99		
8	5	2	31.80	31.17	*20.61	*23.39	10	3	3	15.35	18.30	15.95	*8.96		
8	5	4	15.40	16.15	3.78	15.70	10	3	4	16.80	20.36	*4.74	19.80		
8	5	5	13.97	13.37	13.21	*2.05	10	3	5	20.68	20.03	*19.77	*3.23		
8	5	6	13.82	12.40	*12.07	*2.84	10	3	8	10.74	8.01	*6.56	*4.57		
8	5	7	12.23	14.74	*11.51	*9.21	10	3	9	9.55	2.77	*0.09	*2.77		
8	5	8	14.77	13.99	13.57	3.40	10	4	0	23.27	24.32	24.32	0.00		
8	6	1	20.40	21.68	21.67	*0.78	10	4	1	27.02	26.01	*8.69	24.31		
8	6	2	21.31	23.60	17.26	16.09	10	4	2	24.97	24.97	*24.02	6.84		
8	6	3	17.52	16.16	*6.56	*14.76	10	4	3	17.00	17.07	13.53	10.40		
8	7	0	29.51	31.63	31.63	0.00	10	4	4	33.43	34.13	27.11	*20.75		
8	7	1	29.11	29.83	11.33	27.59	10	4	5	9.63	10.31	*5.66	*8.62		
8	7	2	34.43	33.96	*15.24	*30.35	10	4	6	14.72	13.54	*12.54	*5.11		
8	7	3	10.87	13.00	*12.93	1.34	10	5	0	10.90	4.32	*4.32	*0.00		
8	7	4	9.46	9.01	1.99	8.79	10	5	2	19.53	14.91	14.86	*1.17		
8	7	6	17.96	14.45	*13.92	*3.89	10	5	3	11.18	11.60	11.54	*1.10		
8	7	7	18.55	19.23	*13.88	*13.31	10	5	4	10.55	12.60	*9.01	*8.80		
8	7	8	14.32	11.05	10.76	2.52	10	5	5	20.82	20.55	*19.69	*5.89		
8	8	0	10.76	11.27	11.27	*0.00	10	5	7	12.48	17.14	10.61	13.46		
8	8	1	14.15	12.86	*12.80	*1.23	10	6	2	10.32	7.87	*6.57	*4.33		
8	8	3	9.84	8.70	*0.34	*8.70	10	6	4	13.93	12.03	10.84	*5.24		
8	8	4	11.97	12.11	*8.23	*10.39	10	6	5	12.09	9.42	*8.11	*4.79		
8	8	5	13.15	13.55	*0.08	13.55	10	7	0	10.02	5.21	*5.21	*0.00		
8	8	6	9.94	5.45	*1.55	5.22	10	7	1	11.44	8.58	0.49	*8.57		
8	9	0	35.48	36.34	36.34	0.00	10	7	2	14.27	16.50	11.18	*12.14		
8	9	2	23.94	23.22	*22.61	*5.25	10	7	3	13.96	14.92	14.87	*1.27		
8	9	3	17.34	18.61	*16.91	7.77	10	7	4	20.10	19.68	*13.55	*14.27		
8	9	4	14.46	13.27	13.21	1.20	10	7	5	13.16	12.94	*12.74	*2.24		
8	9	5	9.51	6.09	3.80	4.77	10	7	7	20.48	18.00	10.85	14.36		
8	9	10	10.97	6.01	*4.87	*3.52	10	8	1	16.06	13.82	*6.23	*12.33		
8	10	2	11.44	7.34	*0.52	*7.32	10	8	4	12.94	13.04	2.19	12.85		
8	10	8	11.80	5.11	3.66	3.57	10	9	0	13.04	18.64	*18.64	*0.00		
8	11	0	21.77	23.01	23.01	0.00	10	9	1	11.11	10.01	*8.65	5.03		
8	11	2	12.68	14.43	*14.43	0.38	10	9	3	21.34	21.86	19.97	*8.88		
8	11	3	9.79	7.12	*7.10	0.62	10	9	5	10.03	10.87	*10.85	*0.67		
8	11	4	11.03	8.51	7.97	2.98	10	11	0	10.33	10.32	*10.32	*0.00		
8	15	1	10.13	3.69	2.43	2.77	10	11	1	13.22	11.69	*8.36	8.17		
9	1	0	49.08	50.63	50.63	0.00	10	11	3	13.50	10.11	9.42	*3.66		
9	1	1	33.43	34.54	*8.65	*34.23	10	11	6	12.73	4.25	4.20	0.59		
9	1	2	25.10	29.83	*11.22	*27.64	10	12	0	10.78	6.42	6.42	0.00		
9	1	3	29.09	29.21	*29.19	1.00	10	13	2	10.01	5.05	4.69	1.87		
9	1	4	17.86	18.53	16.09	9.18	11	1	0	15.40	16.84	*16.84	0.00		
9	1	5	38.30	39.69	47.64	28.49	11	1	1	14.34	14.76	*7.78	12.54		
9	1	6	9.56	11.65	*9.94	*6.08	11	1	3	21.24	20.39	19.35	6.42		
9	1	7	9.94	9.80	*9.38	*2.82	11	1	4	22.52	20.98	*13.32	16.22		
9	1	8	13.28	18.71	18.23	4.22	11	1	5	29.47	28.53	*26.91	*9.49		
9	2	0	25.61	26.12	26.12	*0.00	11	1	7	16.25	21.42	17.06	12.96		
9	2	1	33.54	33.36	*29.83	*14.94	11	2	0	23.78	26.62	*26.62	*0.00		
9	2	2	40.89	39.13	*6.17	38.64	11	2	1	27.83	28.62	*1.78	28.56		
9	2	3	12.68	14.26	12.12	*7.51	11	2	2	9.19	11.23	7.48	*8.37		
9	2	4	27.51	30.00	25.75	15.40	11	2	3	9.66	8.75	6.38	5.98		
9	3	0	39.64	43.13	43.13	0.00	11	2	4	11.55	10.52	*8.41	6.32		
9	3	1	26.80	28.92	27.28	9.59	11	3	0	16.16	16.78	16.78	0.00		
9	3	2	33.68	33.67	*35.46	*3.84	11	3	1	24.68	21.79	*18.74	11.13		
9	3	3	24.17	25.80	*23.34	10.99	11	3	2	17.61	15.61	8.19	*13.29		
9	3	4	21.06	17.61	16.22	6.67	11	3	3	30.49	29.32	27.90	*8.99		
9	3	5	22.01	22.29	20.23	*9.36	11	3	4	13.80	14.17	*10.38	*9.65		
9	3	7	19.76	20.03	*13.03	*15.21	11	3	5	18.21	20.36	*20.35	0.64		
9	3	8	11.67	8.39	8.39	*0.21	11	4	0	14.16	11.85	*11.85	*0.00		
9	3	10	10.85	6.66	*5.81	*3.26	11	4	2	9.78	9.19	6.10	*6.88		
9	3	11	11.33	1.56	*1.00	1.19	11	4	3	12.71	13.52	*11.76	6.67		
9	4	0	17.73	18.63	18.63	*0.00	11	4	4	17.47	16.59	*16.59	0.13		
9	4	1	22.05	24.22	*22.92	*7.83	11	4	6	10.22	12.45	11.10	5.63		
9	4	3	17.52	17.23	15.56	7.40	11	5	1	14.71	12.78	*12.61	2.06		
9	4	4	21.98	20.30	19.97	3.68	11	5	2	11.45	12.97	2.47	*12.73		
9	4	6	12.38	14.00	*12.68	*5.92	11	5	3	20.04	20.76	19.21	*7.87		
9	4	8	8.52	3.08	3.45	3.04	11	5	4	12.06	14.03	*4.73	*13.21		
9	5	0	30.46	29.70	29.70	0.00	11	5	5	11.54	11.56	*11.29	2.50		
9	5	1	28.91	26.98	22.25	15.27	11	5	6	11.02	5.08	4.50	2.32		
9	5	2	25.45	25.15	*24.82	4.06	11	6	1	20.38	20.65	3.74	*20.30		
9	5	3	19.61	19.99	*17.81	9.09	11	6	2	10.51	8.48	8.38	*1.26		
9	5	4	14.17	14.84	12.80	7.49	11	6	3	18.59	18.76	*18.64	1.88		
9	5	5	17.14	18.43	12.65	*13.40	11	6	4	19.91	20.56	*20.23	*3.66		
9	5	6	5.53	5.81	*2.95	5.01	11	6	6	12.90	16.20	10.70	12.16		
9	5	7	12.04	16.58	*7.97	*14.53	11	7	0	12.74	11.67	*11.67	*0.00		
9	6	0	9.33	7.73	*7.73	*0.00	11	7	3	10.29	5.06	1.39	4.73		
9	6	1	12.61	11.91	*11.69	2.25	11	7	9	10.03	2.65	*1.79	*1.95		
9	6	2	17.11	12.83	*5.58	*11.55	11	8	2	11.19	13.68	13.11	*3.90		
9	6	3	22.80	22.43	11.17	19.45	11	8	4	17.91	15.85	*15.83	0.90		
9	6	4	14.18	13.33	10.38	*8.38	11	8	5	11.66	11.25	10.07	5.01		
9	6	5	12.51	13.70	*7.37	*7.76	11	8	6	13.13	9.67	8.22	5.09		
9	6	6	21.55	21.28	*17.75	*11.74	11	9	0	9.95	7.44	*7.44	0.00		
9	6	8	15.52	15.01	7.53	12.95	11	9	3	9.64	8.62	*5.56	6.58		
9	6	9	11.21	9.65	*9.61	*9.81	11	9	4	11.87	7.85	2.20	7.54		
9	7	0	10.80	9.59	9.59	0.00	11	9	5	12.51	3.08	*0.52	*3.03		
9	7	2	11.07	5.62	6.36	*5.82	11	9	7	9.69	2.32	2.18	0.79		

11	10	3	10.09	2.68	2.60	0.64
12	0	0	33.34	30.48	-30.48	-0.00
12	0	2	15.51	16.28	15.05	6.19
12	0	3	24.48	25.29	-13.93	21.11
12	0	4	18.29	16.30	-15.73	-4.30
12	0	5	13.03	11.71	4.69	-10.73
12	0	6	13.50	20.23	19.88	3.76
12	0	7	9.93	9.13	-1.75	-8.96
12	1	1	14.77	11.76	11.65	1.61
12	1	2	12.01	13.03	6.13	-11.51
12	1	3	8.91	2.40	-1.33	1.99
12	2	0	17.54	16.87	-16.87	-0.00
12	2	1	9.27	11.12	-9.97	-4.92
12	2	2	12.15	14.44	14.37	-1.37
12	2	3	13.14	13.70	-7.86	11.22
12	2	4	19.58	19.93	-19.93	0.06
12	2	5	10.96	7.31	7.26	0.67
12	2	6	12.48	14.88	13.33	6.62
12	3	1	16.32	13.26	12.72	3.75
12	3	2	10.15	9.94	5.35	-8.37
12	3	4	12.13	13.34	6.41	-11.70
12	3	7	10.64	10.98	-9.63	-5.27
12	3	9	10.38	3.67	-3.06	2.03
12	4	1	17.12	15.99	-11.47	-11.14
12	4	2	16.60	19.29	17.28	-8.58
12	4	3	8.27	2.65	0.88	-2.50
12	4	4	19.09	19.13	-19.08	-1.33
12	4	5	13.10	14.31	6.71	12.63
12	5	1	9.38	8.20	8.19	-0.56
12	5	2	10.39	13.36	-5.48	12.18
12	5	3	17.99	15.29	-15.28	-0.56
12	5	4	11.77	8.21	7.17	-3.99
12	5	5	13.59	12.13	10.34	6.35
12	5	7	10.66	5.84	-4.62	-3.57
12	6	5	10.94	8.15	6.16	5.34
12	7	2	17.99	18.93	-2.31	18.79
12	7	3	12.55	16.04	-15.97	-1.57
12	7	5	11.41	13.52	11.07	7.77
12	8	2	9.93	7.12	-2.29	6.74
12	10	5	9.95	4.15	-3.50	-2.23
12	12	0	9.98	2.31	2.31	0.00
13	1	0	18.47	18.42	-18.42	-0.00
13	1	1	22.92	24.44	22.18	10.27
13	1	2	10.06	11.35	-2.07	11.16
13	1	3	10.42	10.36	-9.52	-4.08
13	1	4	13.13	14.80	7.57	-12.71
13	1	5	10.94	9.72	9.18	-3.20
13	1	7	12.76	13.38	-12.00	-5.92
13	2	0	12.18	9.98	9.98	0.00
13	2	1	20.98	18.66	16.60	-8.51
13	2	2	14.49	13.41	-5.21	-12.35
13	2	4	8.94	7.44	-4.10	-6.21
13	3	1	13.98	11.83	11.63	-2.16
13	3	2	11.25	9.01	6.91	5.78
13	3	3	17.17	14.80	-14.54	-2.77
13	3	4	9.36	0.83	0.02	0.83
13	3	5	9.33	10.75	7.75	7.44
13	4	2	10.65	12.11	-11.10	-4.64
13	5	1	11.05	7.91	6.72	-4.17
13	5	2	9.82	7.73	5.95	4.95
13	5	3	13.23	10.99	-10.84	-1.82
13	5	6	12.01	8.05	-7.84	-1.82
13	6	0	11.55	8.41	8.41	0.00
13	6	1	11.70	10.63	-0.15	10.63
13	6	2	15.12	11.73	-11.24	3.36
13	6	4	12.08	12.57	11.15	5.91
13	8	0	11.20	9.74	9.74	0.00
13	8	1	10.42	8.29	5.93	7.29
13	8	3	9.41	4.86	-2.43	-4.21
13	8	4	10.33	9.03	7.44	5.12
13	10	0	10.06	9.95	9.95	0.00
13	10	5	10.16	3.99	-1.72	-3.61
14	0	0	28.64	26.09	26.09	0.00
14	0	1	11.51	14.12	11.83	7.71
14	0	2	20.53	21.29	-18.65	-13.27
14	0	3	19.15	17.53	10.41	-14.11
14	1	1	9.58	7.76	-1.63	-7.59
14	2	0	16.96	15.47	15.47	-0.00
14	2	1	10.37	10.90	10.45	3.09
14	2	2	14.49	15.11	-13.00	-7.71
14	3	0	11.63	13.78	13.78	0.00
14	4	0	9.75	6.03	6.03	-0.00
14	4	1	10.31	7.05	7.04	-0.37
14	4	2	11.47	9.03	-8.33	-3.49
14	4	3	11.69	12.20	-12.20	0.10
14	4	4	11.17	10.76	3.36	10.22
14	5	1	13.51	12.93	-12.72	-2.33
14	6	3	11.71	5.91	-5.76	-1.34
14	7	2	10.64	5.37	-4.06	-3.52
14	11	0	11.49	7.65	7.65	0.00
15	1	0	13.80	11.90	11.90	0.00
15	1	1	15.69	15.25	-16.00	-8.77
15	1	3	9.48	9.07	8.93	1.56
15	1	6	10.14	7.95	-7.89	-1.01
15	2	1	12.88	10.31	-8.77	-5.42
15	3	1	11.98	11.13	-9.01	-6.53
15	3	3	10.06	7.79	0.01	7.79
15	4	0	12.04	6.53	-6.53	-0.00
15	4	1	10.90	4.93	-4.62	-1.72
15	4	2	10.63	10.00	7.40	6.72
15	6	0	16.46	16.09	-16.09	-0.00
15	6	3	10.69	8.13	8.04	1.19
15	8	0	9.82	10.59	-10.59	-0.00
15	9	2	9.70	3.28	2.14	-2.49
16	0	0	11.62	6.96	-6.96	-0.00
16	0	1	13.05	8.34	-7.94	-2.54
16	0	2	11.89	12.86	12.51	2.99
16	0	3	9.42	4.08	2.35	-3.34
16	2	0	11.94	8.40	-8.40	-0.00
16	2	2	11.81	8.86	6.55	5.97
16	3	3	9.80	6.09	-5.18	-3.21
16	4	0	12.25	7.80	-7.80	-0.00
16	7	1	10.58	9.90	9.78	1.59
18	0	0	10.46	4.42	-4.42	-0.00
18	3	2	11.07	1.25	-0.85	0.91

APPENDIX 3

Computer Program HFIND

```
C          START OF MAIN PROGRAM GEN/HFIND

      COMMON     A(3,3),B(2,4),X(2),Y(2),Z(2)
      REAL       K1,K2,AX(2),BY(2),CZ(2)
      INTEGER ATOM
   19 FORMAT(15X,'CELL DIMENSIONS')
      WRITE(6,19)
C          READ CELL DIMENSIONS
   20 FORMAT(6F10.6)
      READ (5,20)P,Q,R,ALPHA,BETA,GAMMA

      WRITE(6,20)P,Q,R,ALPHA,BETA,GAMMA
C          ALPHA = GAMMA = 90  NOT = TO BETA
      BETA=(BETA/180.)*3.142
      CBETA = COS(BETA)
      SBETA = SIN(BETA)
      PRINT*/,CBETA,SBETA
C          NC = NO OF CALCULATIONS TO BE DONE
      READ (5,21)NC
   21 FORMAT(I5)
       NO=0
      DO 100 I=1,NC
       NO=NO+1
      READ (5,22)((A(J,K),K=1,3),J=1,3)
   22 FORMAT(30X,3F10.6)
C          D1=LENGHT OF BOND 1  D2=LENGHT OF BOND 2
C          DN = DESIRED LENGHT OF H BONDS
C          ATOM = NO OF ATOM AROUND WHICH H ATOMS ARE TO BE FOUND
      READ(5,23)D1,D2,DN,ATOM
   23 FORMAT(3F10.6,I5)
      WRITE(6,120)ATOM
  120 FORMAT(15X,'INPUT FOR ATOM',I5)
  121 FORMAT(3F15.6)
      WRITE(6,121) ((A(J,K),K=1,3),J=1,3)
      WRITE(6,23)D1,D2,DN,ATOM
      DO 10 J=1,3
      A(J,1) = A(J,1)*P+A(J,3)* R*CBETA
      A(J,2) = A(J,2)*Q
   10 A(J,3) = A(J,3)*R *SBETA
      B(1,1) = A(2,1)-A(1,1)
      B(1,2) = A(2,2)-A(1,2)
      B(1,3) = A(2,3)-A(1,3)
      B(2,1) = A(3,1)-A(1,1)
      B(2,2) = A(3,2)-A(1,2)
      B(2,3) = A(3,3)-A(1,3)
      K1 = -0.33326*DN*D1
      K2 = -0.33326*DN*D2
      B(1,4) = K1
      B(2,4) = K2
      CALL HELP
      AX(1) = X(1)/P
      BY(1) = Y(1)/Q
      CZ(1) = Z(1)/R
      AX(2) = X(2)/P
      BY(2) = Y(2)/Q
      CZ(2) = Z(2)/R
      WRITE(6,200)NO,ATOM
  200 FORMAT(10X,'CALCULATION',I6,10X,'ATOM NO IS',I5/26X,'X',18X,
     1'Y',18X,'Z')
   24 FORMAT(20X,F10.4,10X,F10.4,10X,F10.4)
      WRITE(6,24)AX(1),BY(1),CZ(1)
  100 WRITE(6,24)AX(2),BY(2),CZ(2)
      CALL EXIT
      END
```

```
      SUBROUTINE HELP   written by L. Pearson
      COMMON    A(3,3),B(2,4),X(2),Y(2),Z(2)
C
C          A     MATRIX OF CO-ORDINATES
C          B     MATRIX OF VECTORS
C          X     RETURNS THE VALUES OF X
C          Y     RETURNS THE VALUES OF Y
C          Z     RETURNS THE VALUES OF Z
C
           INTEGER I,J,K,IERR
           REAL     PIVOT,T1,T2,Q(3),WK(3),RROOT(2),IROOT(2),MU
C
C          SET UP LINEAR EQUATIONS
         B(1,4) = B(1,4) +A(1,1)*B(1,1) + A(1,2)*B(1,2) + A(1,3)*B(1,3)
        B(2,4) = B(2,4) + A(1,1)*B(2,1) + A(1,2)*B(2,2) + A(1,3)*B(2,3)
C
C          DECOMPOSE MATRIX B USING GAUSS-JORDAN ELIMINATION TO PRODUCE
C          X & Y WITH RESPECT TO Z
                K=2
                DO 2 I=1,2
                     PIVOT = B(I,I)
                     MU = B(K,I)
                     DO 1 J=I,4
                          B(I,J) = B(I,J) / PIVOT
    1                     B(K,J) = B(K,J) - B(I,J)*MU
C
    2                K = K-1
C
C
C          SET UP QUADRATIC EQUATIONS
                T1 = B(1,4) - A(1,1)
                T2 = B(2,4) - A(1,2)
                T3 = A(1,3)
C
                Q(1) = T1*T1 + T2*T2 + T3*T3 - 1
                Q(2) =-2*(T1*B(1,3)+T2*B(2,3)+T3)
                Q(3) = B(1,3)**2 + B(2,3)**2 + 1
C
C          SOLVE QUADRATIC
                CALL POLRT(Q,WK,2,RROOT,IROOT,IERR)
C
C          CHECK FOR ERRORS
                IF(IERR)4,4,3
    3           WRITE(6,100)IERR

  100                FORMAT(' IERR=',I2)
                     CALL EXIT
C          SUBSTITUTE Z VALUES TO OBTAIN X & Y VALUES
    4           Z(1) = RROOT(1)
                Z(2) = RROOT(2)
                X(1) =-B(1,3)*Z(1) + B(1,4)
                X(2) =-B(1,3)*Z(2) + B(1,4)
                Y(1) =-B(2,3)*Z(1) + B(2,4)
                Y(2) =-B(2,3)*Z(2) + B(2,4)
C
C
      RETURN
      END
```