STRUCTURES
OF
WERNER CLATHRATES

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by

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This work is dedicated to my parents.

Αυτή η δουλιά αφιερώνεται στούς γονείς μου

ABSTRACT

X-ray crystallographic studies have been used to elucidate the structures of two new Werner clathrates.

$Ni(NCS)_2(4\text{-phenylpyridine})_4.4$dimethylsulphoxide is triclinic with space group $P\bar{1}$, a = 25.21(1)Å, b = 12.217(6)Å, c = 10.242(5)Å, α = 112.35(2)°, β = 84.12(2)°, γ = 90.75(2)° and Z = 2. The guest molecules, DMSO, are located in channels running parallel to the Z axis.

$Ni(NCS)_2(3\text{-methylpyridine})_4.$chloroform is orthorhombic with space group Fddd, a = 26.28(1)Å, b = 24.35(1)Å, c = 21.47(1)Å, and Z = 16. The chloroform molecule is disordered, lying on a two-fold axis.

Stoicheiometric characterization of the clathrates was determined using various chemical techniques, including mass spectroscopy, proton nuclear magnetic resonance and complexiometric titration.

The clathrating phase of the second clathrate was investigated by guest-loss studies on a McBain balance followed by X-ray powder photography.

Host-guest non-bonded interactions of both clathrate compounds were studied using atom-pair potentials.

CHAPTER 1

CHAPTER ONE

INTRODUCTION

The bonding of chemical species resulting from "normal" chemical reactions has always been defined explicitly in terms of ionic, covalent or coordinate covalent bonds[1]. In addition to these compounds there exist molecular compounds which stereospecifically form "complexes" with a number of inorganic and organic substances without chemical bonds. The understanding of their chemistry is relatively new, although these "complexes" have been known for over 100 years. The hydrate of chlorine was first synthesized in 1811 by Davy[2]; a 3:1 adduct of quinol and hydrogen sulphide was prepared by Wöhler[3] in 1849.

It was only as late as 1948 that their unusual structural properties were characterized by Powell[4] who suggested that these combinations of compounds should be described as "clathrate" compounds, derived from the Latin word "clathratus" meaning enclosed or protected by crossbars of a grating. A year later, in connection with studies to clarify the structure of the urea "complexes", they were termed "inclusion" compounds[5].

Molecular inclusion compounds have been described as combinations where one component, commonly named the "host", owing to its suitable steric properties and partially also polarity, is able to enclose spatially atoms or molecules of a second component, commonly called the "guest".

An essential characteristic of the host is its ability to form a structural framework containing spaces with large enough dimensions to house the prospective guests. In turn, the spatial arrangement of the guest molecule must correspond to the dimensions of the free cavity. The interaction between host and guest is at the level of van der Waals forces and corresponds to the energetically most suitable mutual arrangement[6].

The great diversity of molecular inclusion compounds sometimes makes it very difficult to classify them unambiguously. In general, they may be sub-classified as the layer (or intercalate) type where the guest component is situated between bands of host structure; the channel type, in which the guests are accommodated in continuous canals running through the crystal; and the true clathrate type in which the guest molecules are imprisoned in discrete closed cavities or cages[7]. Some examples will be described before their properties are further discussed.

Intercalates or Layer-Type Compounds

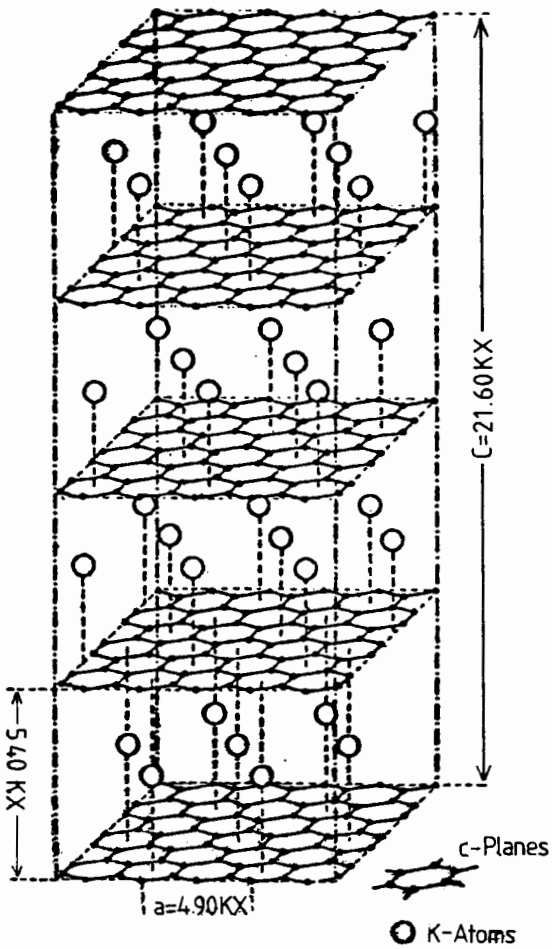


Figure 1.1

Graphite, an allotrope of carbon, is one of the simplest compounds having a layered structure[8]. The weak van der Waals interlayer forces of the hexagonal graphite lattice allow atoms or molecules such as C_8K, K, CrO_3, SbF_5 and $AlCl_3$ to penetrate between the layers. The interlayer spacing imposes a selectivity which is dependent on the size of the molecule or the stereochemistry around the reaction centre[7].

Channel-Type Compounds

Schlenk[5] discovered that urea crystallizes in a hexagonal polymorph to form hollow channels large enough to accommodate hydrocarbon molecules. Hydrogen bonds between the hydrogen of the NH_2 groups and the oxygen of the adjacent urea molecules account largely for the stability of the complex. The urea host lattice can accommodate only straight chain hydrocarbons, whereas the channels formed by thiourea can accommodate both straight chain and branched chain hydrocarbons. This difference in selectivity between the two host lattices is attributed to differing dimensions of the two. Thirourea is stable only in the presence of a guest molecule, and it offers a unique situation when forming an inclusion compound with monochlorocyclohexane. The axial conformer is the more abundant, whereas in liquid and gaseous phases the equatorial conformer is more abundant. The solid phase consists of the equatorial conformer alone.

The oldest of the recorded inclusion compounds are those of the choleic acids which form channel structures resembling, in some respects, the urea-hydrocarbon complexes[1]. The more commonly known choleic acid complexes are those of desoxycholeic acid. These include some hydrocarbons and many esters, alcohols, carboxylic acids, phenols, ethers and alkaloids.

Typical of the channel inclusion compounds are the cyclodextrins (cycloamyloses), occasionally called Schardinger dextrins because they were originally prepared by him in 1903[9]. They are produced by the enzymatic partial hydrolysis of starch, which yields torus-shaped molecules made up of different numbers of α-1,4 -linked D-gluco-

pyranose units. The most common, comprising six, seven or eight of these units are termed α-, β- and γ-cyclodextrins respectively (see Figure 1.2). Stacking of these carbohydrate rings on top of each other produces a continuous channel running down the middle of the crystal, in which organic molecules such as trichlorethylene in α-cyclodextrin, toluene in β-cyclodextrin or bromobenzene in γ-cyclodextrin, are held by van der Waals forces. Most studies of cyclodextrin inclusion compounds have been done in aqueous solution, though complexation has also been found for β-cyclodextrin in non-aqueous solvents. Recently, numerous X-ray studies with various guests have revealed that α-cyclodextrins can form both channel-tyoe and cage-type inclusion compounds[7].

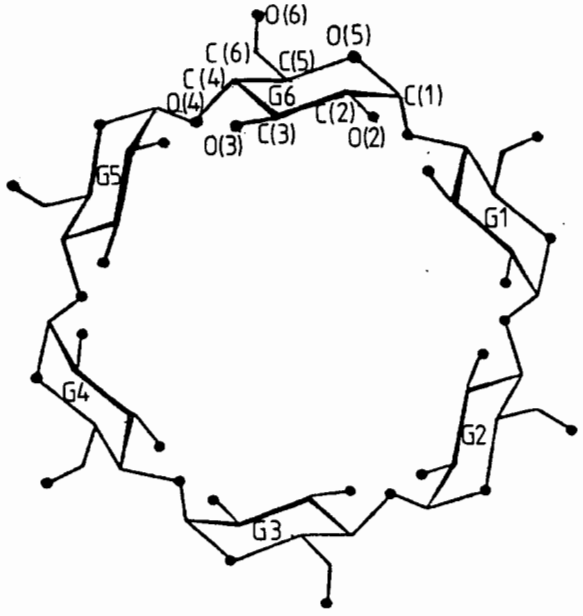


Figure 1.2 α**-Cyclodextrin**

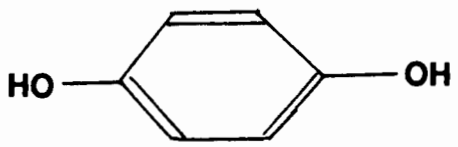
In contrast to systems discussed earlier, the inclusion-forming ability of cyclodextrins involving host-guest interactions is found both in the solid state and in solution, resulting in their investigation as biomimetic systems.

Cyclodextrins and their inclusion compounds have a large diversity of applications. To name but a few:

- mono-substituted cyclodextrins have been prepared in connection with enzyme model studies;
- α- cyclodextrin is an efficient separating agent for o-, m-, and p-cymene;
- the nitroglycerine inclusion compound of β-cyclodextrin can be used as an explosive;
- the cyclohexylamine complex of β-cyclodextrin is used in rust prevention;
- the CO_2 clathrate of α-cyclodextrin can serve as a baking powder.

Cage-Type Inclusion Compounds

β-Hydroquinone (quinol) clathrates are of great historical significance as it was the pioneering X-ray work of Palin and Powell [10, 11, 12] on these compounds that led to the introduction of the name "clathrate compound".



β-Hydroquinone forms discrete spherical cages by the linking of the molecules through their OH-groups. Six oxygen atoms of six different molecules form hydrogen-bonded hexagons which can enclose completely only small guest molecules with one guest molecule per cavity, e.g. Ar, Kr, C_2H_2, HCl. Refinement of the hydroquinone-hydrogen sulphide clathrate by Ho and Mak[13] provided an accurate description of the undistorted -hydroquinone host lattice. As far back as 1948, Powell [14] further showed that if larger molecules are included, the hydro-

quinone lattice is distorted to form oblong cavities. This distortion increases in the series CH_3OH, SO_2, CO_2 and is extreme in the case of CH_3CN. (see Figure 1.3). Thus quinol clathrates enable us to study small isolated guest molecules.

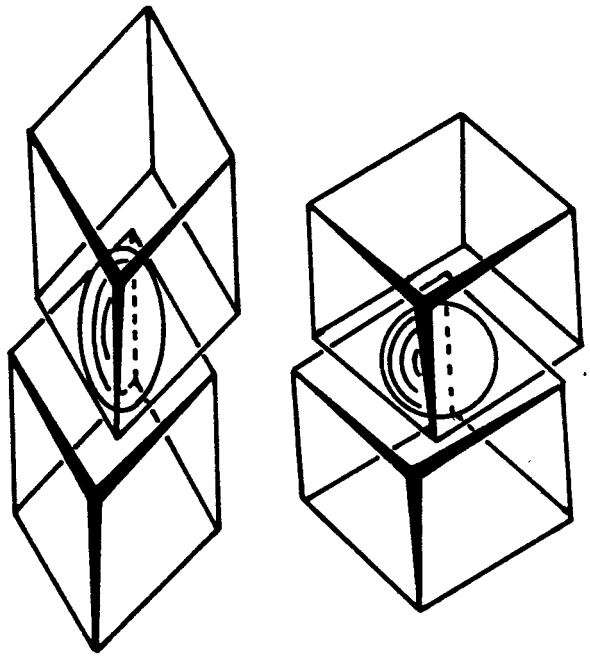


Figure 1.3 Distortion of the β-hydroquinone lattice

Another well-studied cage-type inclusion compound is 4-p-hydroxyphenyl-2,2,4-trimethylchroman, commonly known as Dianin's compound since it was first prepared by him in 1914[15]. It contains an hexagonal unit of hydrogen-bonded OH groups, which is also common to quinol, but the cavity formed is larger. It is therefore able to accommodate more than one guest molecule thus presenting the opportunity to study guest-guest interactions. The cavity size can be varied by modifying the structure, for example, by removing one of the *gem* dimethyl groups, by replacing the ether oxygen by sulphur, or by replacing the OH group by SH.

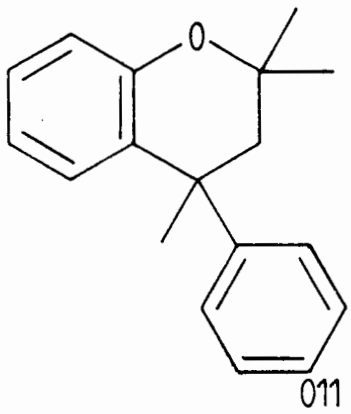


Figure 1.4

Recent X-ray studies have confirmed the cage structure for Dianin's compound with ethanol, chloroform[16] and n-neptanol complexes. All guest molecules in the above studies exhibited disorder.

Dianin's compound can be used as a matrix for studying free radicals [17], or in the ready sorption of gases such as Ar, Kr, Xe and CH_4[18].

Phenol itself forms clathrates, in which the basic feature of the host structure is again the linking of the OH groups of six phenol molecules by hydrogen bonds such that the oxygen atoms form a hexagon, alternate phenyl groups pointing above and below this hexagon[7]. Two types of centrosymmetric cage are formed, one large with an effective length of $\approx 15\text{Å}$ and free diameter of 4.0-4.5Å, and one small with a free diameter of $\approx 4.5\text{Å}$. Suitably sized guest molecules such as noble gases, or other volatile species, are included in phenol or simple substituted phenols such as p-fluorophenol, m-fluorophenol, o-fluorophenol, p-chlorophenol, p-cresol, and p-bromo, ethyl-, t-butyl-, and phenyl-phenols.

An intermediate class of clathrates are the zeolites which are macromolecular inclusion compounds[1]. These are essentially crystalline structures in which the basic host framework consists of silicon-oxygen or aluminium-oxygen tetrahedra. A three-dimensional network is formed in which the cavities are interconnected by channels. Zeolites have the ability to hold certain molecules loosely within their cavities, normally water molecules, which can be removed by heating the compound under reduced pressure. These interstices can then be permeated by various gases, vapours or dissolved compound molecules. Of most of the inclusion compounds mentioned here, zeolites are the only ones which are completely stable in the absence of guest molecules, and which allow easy migration of guests from one cavity to the next through the channels. Besides the naturally-occurring zeolites, many others have been synthesized. The synthesis is a controlled one in which production of a certain zeolite is very well worked out. The different modifications of the zeolites have numerous industrial applications. They are widely used to upgrade gasoline, to dry gases on a commercial scale, to separate hydrocarbon mixtures and, of course, commonly as ion exchange media.

This latter example shows how the classification of inclusion compounds is not precise. Depending on the shape and size of the guest molecules, some compounds may be regarded either as zeolitic or clathrate-type. Others may be classified as pseudo-layer (zeolitic layer structure) being an intermediate between the layer-type and the zeolitic type. It is for this reason that the term "clathrate" is used very often to describe all molecular inclusion compounds.

As mentioned earlier in this chapter, the clathration process is selective towards the size and shape of possible guests, but not necessarily if they differ in physico-chemical properties[19]. Interest in the clathratogenic properties has lead to extensive investigations on a class of coordination copounds having the general formula MX_2A_4 (where M= Ni, Co, Fe, Mn, Zn, Cu; X= Halide or SCN, CNO, NO_2; A= pyridine base, α-alkylarylammine, ester or amide of nicotine, etc). Prior to the extended study of these complexes the only reported inorganic complex able to form clathrates was $Ni(NH_3)(CN)_2$[20].

These constitute a new family of complexes which have been named "Werner clathrates". The term "clathrates" is misleading since these compounds display characteristics of both the channel and the cage-type inclusion compounds.

The host complex may adopt three different modifications. The α-phase is the "non-clathrating" modification where the molecular packing of the host molecules is unable to form any suitable voids in the crystal lattice due to reasons such as steric or electronic interactions.

When energy situations in the system are favourable, the "clathrating" β-phase is formed:

$$\alpha\text{-phase} + \text{guest} \rightarrow \beta\text{-phase clathrate}$$

A γ-modification is also possible where the cavities formed are of the layer-type.

In 1956, Schaeffer and coworkers[21] managed to prepare many new complexes of inorganic salts and basic nitrogen compounds, and were very successful as far as separation of mixtures of isomers is concerned. This new class of clathrates demonstrated a sharp selectivity towards certain organic molecules, the selectivity being based, apparently, on the shape rather than on the molecular volume occupied by the organic moiety. Examples of isomers that were effectively separated are xylenes, cymenes and methylnaphthalenes.

In 1960 Kemula and Sybilska[22] introduced "clathrate chromatography" to analytical chemistry as an effective and important method in the study of inclusion compounds. Quantitative analysis of mixtures was effectively achieved.

An interesting example is one given by Allison and Barrer[23] who discovered that the α- to β-phase transformation of $Co(NCS)_2$(4-ethylpyridine)$_4$ was effected only by o- and p-Xylene and not by m-Xylene. Connected with the shape of ligand are, of course, steric and electronic effects.

One of the most versatile Werner complexes that has been prepared is $Ni(NCS)_2(4\text{-}MePy)_4$. Extensive studies, both analytical and crystallographic, have been done on this particular complex, which is a typical MX_2A_4 complex, to demonstrate the clathration process, and to study the unusual properties of the Werner clathrates in general.

Accumulated investigations on the $Ni(NCS)_2(4\text{-}MePy)_4$ clathrates led to certain rules regarding guest inclusion into a host lattice.

In general, for guest molecules:

(i) Only compounds containing at least one aromatic ring are clathrated;

(ii) Very polar or reactive substituents on the ring must be avoided;

(iii) Accumulation of polar groups diminishes clathrating ability e.g. dichlorobenzenes are clathrated, but not tricholorobenzenes;

(iv) Accumulation of bulky groups makes the compound less easily clathrated e.g. ethylisopropylbenzenes may be clathrated, but not diisopropylbenzenes;

(v) Aromatic guests with electronegative groups must be avoided, since the aromatic nucleus of the amine of the Werner complex is an acceptor of π-electrons from the aromatic nucleus of the guest.

The substituents on the amine group of the host complex must also be considered in the preferential clathration of isomers. For example, in the clathration of xylenes by substituted α-methylbenzylamines, the complexes in which the amine of the host is substituted on p-or m-positions giving a negative inducing effect (e.g. F, Cl, Br, I, NO_2) display para-selectivity towards the guest. When the substituent on the host gives a positive inducing effect (e.g. CH_3, C_2H_3) the complex displays ortho-selectivity towards the guest.

Clathrated compounds must fit tightly in the cavities of the host lattice in order to give maximum cohesion with the aid of van der Waals forces. Sometimes there is conflict between steric and electronic forces and it becomes difficult to foresee selectivities.

Smith[24] has analyzed the equilibrium solid phases given by the known mixtures of $Ni(NCS)_2(4\text{-MePy})_4$ as host with the pairs:

p-Xylene - ethylbenzene
p-Xylene - toluene
ethylbenzene - toluene
p-Xylene - p-dichlorobenzene

In each case the molar ratio of host to guest was unity. They found the order of clathration to be

p-Xylene $\succ$ ethylbenzene $\succ$ toluene and
p-Xylene $\succ$ p-dichlorobenzene

They proved that these selectivities were attributed to the varying solubilities of the host in the different guests, and also to the different polarizabilities of the guests.

Many complexes have been synthesized which do not form clathrates. The study of these, too, is important since it leads to a better understanding as to why some complexes form the clathrating β-phase and why others do not.

Allison and Barrer[23], on investigating complexes with a large variety of ligands and transition metals, discovered that when the ligands were pyridine, 3-methylpyridine and 4-propylpyridine, the α-form did not form any porous β-structure and thus no sorption of any guest molecule could occur.

Examples of host complexes which do not form the β-phase are $Ni(NCS)_2(4\text{-vinylpyridine})_4$ and $Co(NCS)_2(4\text{-vinylpyridine})_4$[25, 26, 27]. The lack of clathrating ability of these complexes is probably connected

to the presence of the vinyl group (-CH=CH_2 attached to the pyridine ring) which prevents host-guest interaction.

When compounds form crystalline structures, large spaces in the molecular packing are avoided. Residual attractions between the molecules bring about a closest packing so that the molecules are in their lowest state of potential energy. However, when a guest species is in solution with the host complex, the driving force for clathration is the geometry of the guest molecule and flexibility of the host molecule, and their ability to form an inclusion compound having low potential energy. Host-guest interactions are essential for clathration but must be at the level of van der Waals forces.

Structural investigations have revealed that the clathrating ability of the complex is connected to the freedom of rotation of the Ni-N (pyridine) bond[25]. This flexibility allows the pyridine rings to adapt the shape of the cavity formed by the host lattice in order to accommodate guest molecules - provided the potential energy of the system is favourable.

Table **1.1** lists some of the Werner clathrates that have been formed with the complex $Ni(NCS)_2(4\text{-}MePy)_4$.

Tetragonal $I4_1/a$ β-$Ni(NCS)_2(4\text{-}MePy)_4$ is the most studied sturcture of those listed above. Most clathrates of this host forming a 1:1 ratio of host-guest seem to fulfil these symmetry requirements and it was then assumed that any structure with $I4_1/a$ space group was in the β-modification. It has since been proven that other space groups for this host complex have been discovered.

Crystal cell parameters are of the same order of magnitude indicating that the molecular framework is the same for all these clathrates, thus implying that the guest species could be directly exchanged for another favoured guest without considerable host breakdown. The volume difference can be explained by the fact that the dimensions of the spaces created in the host lattice are greatly dependent on the type and concentration of guest. It has been observed by Lipkowki and

Majchrzak[28] that as guest is absorbed or desorbed, there is a significant β-lattice dilatation or contraction; this may reach to as much as 10% of the total volume of the crystals.
Similarly molecular packings in the triclinic $P\bar{1}$ structures where the guest are p-terphenyl, 2-methylnaphthalene and 2-bromonaphthalene are almost the same[29, 30].

It seemed from all the above studies that for the tetragonal crystal structures a zeolitic rather than a clathrate type could be attributed to their molecular packing. Similarly the molecular packing of the other tabulated structures can be described as being of the zeolitic-layer type.

The above investigations revealed that in clathrate lattice formation, the host conformation depended on the geometry of the guest molecule. Experimental results agreed well with the hypothesis that the host complex, by means of pyridine ring rotation, can adjust its shape to close packing requirements in clathrate crystals.

Generally, the geometry of the inclusion centres is of great importance, especially when considering the clathration of mixtures of guest molecules. Each type of cavity can show selectivity with respect to a given mixture of possible guests.

Structures with differing types of channels were observed by Lipkowski[31]. The crystal structure of $Ni(NCS)_2(4\text{-}MePy)_4$ with naphthalene (1:2), (monoclinic C2/c), displayed layer-packing in which three different patterns were distinguished: two cavities have two-fold axial symmetry, occupied by two well-ordered naphthalene molecules arranged alternately parallel and perpendicular to the two-fold axis; the third cavity is centrosymmetric and is occupied by two disordered naphthalene molecules arranged in centrosymmetric pairs.

Where the guest is 2-methylnaphthalene (1:2), (triclinic $P\bar{1}$), one type of cavity has been found[29], while in the 1-methylnaphthalene[32] and o-Xylene[29] clathrates (1:2), (monoclinic $P2_1/C$), there are two types of cavity.

Sitarski and Lipkowski[34] have attempted a mathematical analysis for the desorption of a gas from the clathrate structure . Their results were based on experiments on the desorption of p-Xylene from $Ni(NCS)_2(4\text{-}MePy)_4$. They divided the desorption process into the following steps:

(1) Release of the guest molecule from the cavity in preparation for diffusion;
(2) Diffusion to the crystal surface;
(3) Desorption from the crystal surface

From these studies one could determine the rate-determining step and hence the enthalpy of clathration[19].

$$\Delta H_{clathr} = -\Delta H_{sorp} + \Delta H_{\alpha\rightarrow\beta} + H_{subl,evapn}$$

where

$\Delta H_{\alpha\rightarrow\beta}$ = enthalpy of $\alpha\rightarrow\beta$ phase transition,
$\Delta H_{subl,evapn}$ = enthalpy of solid (liquid) guest sublimation (evaporation)
ΔH_{sorp} = enthalpy of sorption of gaseous guest by the clathrate β-phase

Thus the energy of bonding the guest to the host lattice (ΔH_{sorp}) could be determined if the phase transition were known, but since dilatation/contraction occurs during sorption/desorption of guest in the β-phase, there is a change in molar volume, which is characteristic to each species and thus the term $\Delta H_{\alpha\rightarrow\beta}$ cannot be assumed constant.

It can only be expressed as a function of the molar volume of the β-phase:

$$\Delta H_{\alpha\rightarrow\beta} \longrightarrow \Delta H_{\alpha\rightarrow\beta_0} + \Delta H_{\beta_0\rightarrow\beta_1}$$

where β_0 and β_1 are the "empty" and "full" clathrates respectively, and $\Delta H_{\alpha\rightarrow\beta_0}$ is independent of the guest species.

A direct X-ray proof is difficult to obtain because ony a few least-stable β-clathrates allow desorption of the guest component rapidly enough to prevent the β⟶α transformation from occurring[35].

Extensive studies are yet to be done on systems where the host molecule is other than the traditional $Ni(NSC)_2(4\text{-}MePy)_4$.

The progress of this work in general, is towards the design and synthesis of new clathrate host materials in order to obtain and accumulate more structural information on selected clathrates, and the nature of host-guest and guest-guest interactions[36, 37]. The most powerful tool in their structure determination is X-ray crystallography. A complete overall study of the clathration process is required so that host lattices can be synthesized which have preferential selectivities towards isomers, enantiomers and conformers.

TABLE 1.1 LATTICE PARAMETERS OF $Ni(NCS)_2(4\text{-}MePy)_4$ AND SOME OF ITS CLATHRATES [38, 39, 40]

Type of Packing	Guest	Space Group	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	Host:Guest Molar ratio
Channel		Tetragonal							
	Benzene	$I4_1/a$	17.02	17.02	23.18	90	90	90	1:1.05
	Toluene	$I4_1/a$	-	-	-	-	-	-	1:0.90
	p-Xylene	$I4_1/a$	16.98	16.98	23.62	90	90	90	1:0.88
	p-Cymene	$I4_1/a$	17.10	17.10	23.84	90	90	90	1:0.77
	4-MePy	$I4_1/a$	17.09	17.09	23.44	90	90	90	1:1
	p-dichlorobenzene	$I4_1/a$	17.30	17.30	22.68	90	90	90	1:1
	methanol	$I4_1/a$	16.99	16.99	22.29	90	90	90	1:1.83
	p-, m-, o-dinitrobenzene	$I4_1/a$	-	-	-	-	-	-	1:1
	m-Xylene	$I4_1/a$	17.28	17.28	28.87	90	90	90	1:1
Layer		Monoclinic and triclinic							
	Naphthalene	C_c	16.27	16.46	31.93	90	89.3	90	1:2
	1-Me-Naphthalene	$P2_1/c$	11.53	11.89	32.85	90	94.3	90	1:1.51
	2-Me-Naphthalene	$P\bar{1}$	11.31	9.58	11.66	115.5	82.0	108.7	1:1.73
	1-bromonaphthalene	$P2_1/c$	-	-	-	-	-	-	1:2
	2-bromonaphthalene	$P\bar{1}$	11.31	9.54	11.76	115.9	81.7	109.6	1:2
	o-Xylene	$P2_1/c$	11.48	11.49	32.72	90	96.6	90	1:2
	p-terphenyl	$P\bar{1}$	11.25	9.56	10.73	83.3	80.7	63.2	1:1
	bromobenzene	P_{nma}	16.51	15.74	15.64	90	90	90	1:2.02
Cage		Hexagonal							
	p-nitrotoluene	-	27.63	27.63	11.16	-	-	-	1:0.60
	m-nitrotoluene	-	27.98	27.98	11.09	-	-	-	1:0.60
	o-nitrotoluene	-	27.70	27.70	11.21	-	-	-	1:0.60
	m-bromonitrobenzene	R3(?)	-	-	-	-	-	-	1:0.66
	o-bromonitrobenzene	R (?)	55.26	55.26	11.08	-	-	-	-
	chloronitrobenzene	-	-	-	-	-	-	-	-
	α-phase	$P2_1/c$	19.8	9.67	16.8	90	117.1	90	

CHAPTER 2

CHAPTER 2

GENERAL EXPERIMENTAL AND COMPUTATIONAL PROCEDURES

INTRODUCTION

This chapter comprises a general summary of the procedures used in the identification of the compounds being investigated, and the X-ray crystallographic methods used in the determination of their crystal structures.

2.1 CRYSTAL PREPARATION

Host complexes were prepared by the method of Schaeffer *et al* [21] as follows:

To 2.00g (0.0084 mol) of metal chloride dissolved in 12ml H_2O was added 1.635g (0.0168 mol) of KSCN. 0.0336 mol of substituted pyridine ligand was added slowly and with constant stirring to the resulting solution. As the ligand was added to the metal solution a precipitate formed. Addition was extended over a period of 5 minutes, and the entire operation carried out at room temperature. After all the ligand was added, the mixture was stirred for an additional 15 minutes to allow the system to equilibrate, and was then filtered. The residue was air dried for 24 hours.

Clathrate complexes were prepared by the "solution" process, as described by in the same paper[21], with minor variations, as follows:

Solid host complex was dissolved in a suitable solvent, the solution being as concentrated as possible, and heated to boiling point. It was often necessary to add a minimal trace of pyridine ligand to obtain a clear solution. The chosen guest was added to this hot solution in more than 5 molar excess. The solution was allowed to stand at room temperature for approximately 5 days in which time the clathrate product crystallized. These crystals were kept sealed under

their mother liquor to prevent crystal deterioration by guest desorption on exposure to air.

2.2 THE CHARACTERIZATION OF THE COMPOUNDS

Microanalysis was employed to estimate the carbon, hydrogen and nitrogen content of both the host complexes and the clathrate compounds, to determine their stoicheiometric compositions.

To determine the stiocheiometry of the clathrates, to identify the guest species and study the structures, further methods included:

density measurements
mass spectroscopy
proton nuclear magnetic resonance
volumetric analysis by complexiometric titration
guest desorption measurements
X-ray powder photography

All crystals used in quantitative determinations were dabbed dry and cleaned on the surface of any adhering mother liquor.

2.3 PRELIMINARY X-RAY ANALYSIS

Single crystals, which extinguished uniformly under plane polarized light, were selected and sealed in Lindemann capillary tubes containing mother liquor to prevent their deterioration in air. A two-circle optical goniometer was used for alignment.

Preliminary crystallographic information was obtained from oscillation and Weissenberg (zero-layer and upper-layer) photographs, which were taken using a non-integrating Stoë (Heidelberg) goniometer, and a camera with radius 28.65 mm. Nickel-filtered CuK_α X-ray radiation (λ= 1.5418 Å) was generated by a Philips X-ray generator (PW1120) operating at 0.8 kW (20 mA and 40kV). X-ray films (3M medical) were processed using Kodak X-ray developer and fixer.

Approximate cell dimensions and space group symmetries were obtained from analysis of the oscillation and Weissenberg photographs. These were confirmed by the diffractometer data.

2.4 DIFFRACTOMETER DATA COLLECTION

Suitable single crystals, mounted with mother liquor in sealed Lindemann capillary tubes, were sent to Mr J. Albain at the National Physical Research Laboratory (N.P.R.L.) at the Council for Scientific and Industrial Research (C.S.I.R.), Pretoria, for diffractometer data collection.

The relative intensities of the reflections were measured on a Philips PW 1100 computer-controlled four-circle diffractometer in the ω-2θ scan mode. A Philips PW1130 X-ray generator operating at 20mA and 50kV (1kW) was the source of the graphite monochromated MoK_α radiation, λ= 0.7107Å. The data collections were carried out at room temperature.

Accurate cell parameters were obtained by a least-squares analysis of the χ, ϕ and 2θ angles of 25 standard reflections accurately centred on the diffractometer.

To monitor instrumental stability and crystal decomposition during the three-dimensional intensity data collection, three standard reference reflections were measured periodically.

Reflections were considered "observed" if the relative integrated intensity I_{rel} exceeded $2\sigma I_{rel}$, where the standard error I_{rel} is calculated from:

$$I_{rel} = [N_{pk} + N_{bg} + N_{instr}]^{1/2}$$

where,

N_{pk} = gross peak count for a specific reflection
N_{bg} = background count measured on each side of the peak
$N_{instr} = [0.02\ (N_{pk} - N_{bg})]^2$

Lorentz polarization corrections were automatically applied to all the reflection data.

2.5 COMPUTATION

Crystallographic calculations and subsequent structure refinement were performed using the integrated program SHELX76[41]. Facilities of this program that were utilised include:

data reduction,
rejection of systematic absences,
automatic centrosymmetric direct methods,
full-matrix least-squares refinements,
geometric positioning and constrained refinement of hydrogen atoms,
bond length constraints and refinement,
analysis of variance,
weighting scheme optimisation,
various Fourier syntheses, and
structure factor listings.

Agreement between the observed and calculated reflection data is described in terms of the residual index, R[42], which is defined as

$$R = \frac{\Sigma|\Delta F|}{\Sigma|F_o|} = \frac{\Sigma\big||F_o| - |F_c|\big|}{\Sigma|F_o|}$$

and for a "well-behaved" structure, which is fully refined, $R < 0.05$. However, with structures having high thermal parameters or partial disorder, one generally accepts $R \approx 0.10$.

Upon introduction of a weighting scheme as a measure of the reliability of the observation,

$$R_\omega = \frac{\Sigma\omega^{\frac{1}{2}}|\Delta|}{\Sigma\omega^{\frac{1}{2}}|F_o|}$$

where

$$\omega = \frac{k}{[\sigma^2(F) + gF^2]}$$

k was redetermined after each structure factor calculation. The value of g was chosen to give the smallest variation of $\omega\Delta^2$ with the magnitude of F_c.

After the final refinement, an analysis of variance was computed to confirm the effectiveness of the weighting scheme. A final low value of R, as well as a low shift/e.s.d. ratio of each thermal parameter indicate an accurately-refined structure.

Atomic radii used were those of Pauling[43]. Scattering factors for all non-hydrogen atoms were from Cromer and Mann[44], and for hydrogen atoms from Stewart, Davidson and Simpson[45].

Least-squares planes and torsion angles were calculated using the program XANADU[46].

The plotting program PLUTO[47] was used for drawing the individual molecules and molecules in their crystalline arrangements, to study molecular packing.

The program EENY[48] was used to study the potential energy environment of the molecules in the crystal.

All computations were carried out on the UNIVAC 1106 computer at the Computer Centre of the University of Cape Town.

CHAPTER 3

CHAPTER 3

THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(ISOTHIOCYANATO)TETRA (4-PHENYLPYRIDINE)NICKEL(II).4DIMETHYLSULPHOXIDE

3.1 SYNTHESIS AND CHEMICAL CHARACTERIZATION

Synthesis

The host complex $Ni(NCS)_2(4\text{-phenylpyridine})_4$ was synthesized using the method described in Chapter 2.

The clathrate crystals were formed as follows:

0.80g (0.00100 mol) of $Ni(NCS)_2(4\text{-phenylpyridine})_4$ was dissolved in 30ml dimethylsulphoxide (DMSO) and heated to boiling point. A spatula-tip of solid 4-phenylpyridine (4-PhPy) was added to produce a clear solution. To this green solution was added 3.0 ml (0.02453 mol) m-Xylene, the intended guest species. The solution was allowed to cool to atmospheric temperature. Purple-blue diamond-shaped crystals of $Ni(NCS)_2(4\text{-PhPy})_4$ - DMSO formed within one day. These were kept under mother liquor to prevent deterioration in air.

Analyses

Microanalysis

Elemental analysis was carried out to determine the percentages of carbon, hydrogen and nitrogen. If the clathrate formed were "empty", i.e. no guest species present, the analysis would have shown percentages for the host complex $Ni(NCS)_2(4\text{-PhPy})_4$, which are theoretically 69.40%C, 4.60%H and 10.60%N.

However, analysis found:
57.80%C, 4.60%H and 7.75%N,
which does not even agree with theoretical percentages had the clathrate been $Ni(NCS)_2(4\text{-PhPy})_4$.m-Xylene, i.e. 71.91%C, 5.14%H and 9.32%N.

The results therefore suggest that some other clathrate species had been formed. Combined with other chemical investigations, the guest was identified as dimethylsulphoxide, the solvent used in the preparation, and elemental percentages confirmed a ratio of four guests (DMSO) per host molecule, i.e. host:guest = 1:4.

Results	57.80%C	5.45%H	7.75%N
Theoretical for host:guest = 1:4	58.60%C	5.46%H	7.60%N

Density Measurements

The density of the clathrate crystals was determined by the flotation method using saturated potassium iodide (ρ = 1.63 $g.cm^{-3}$) and water. This revealed a density of D_m = 1.24 $g.cm^{-3}$.

Crystallographic analysis determined the number of host molecules per unit cell as being two. The number of guest molecules may be calculated from the formula:

$$Z_h(M_h) + Z_g(M_g) = ND_m abcK \times 10^{-24}$$

where Z_h = number of host molecules per unit cell
M_h = molecular weight of host ($g.mol^{-1}$)
Z_g = number of guest molecules per unit cell
M_g = molecular weight of guest ($g.mol^{-1}$)
N = Avogadro constant
D_m = measured density ($g.cm^{-3}$)
$abcK$ = Volume of unit cell ($\mathring{A}^3$)
$K = (1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2}$[42].

With values of Z_h = 2, M_h = 795.67$g.mol^{-1}$, M_g = 78.13$g.mol^{-1}$, D_m = 1.24$g.cm^{-3}$, and $abcK$ = 2900.46$\mathring{A}^3$, the number of guest molecules, Z_g, was calculated to be 7.36, giving a host of guest ratio of 1:3.68, from which we could confirm with near certainty that there were four DMSO molecules per host molecule in the unit cell.

Using the above formula, the calculated density, D_c, was evaluated using $Z_g = 4$. The answer was $D_c = 1.27\ g.cm^{-3}$.

Mass Spectroscopy[49]

The application of mass spectroscopy provides a useful means of identifying the guest species present in the structure. Mass spectrograph data obtained from the different fragments in the ionization process provide information on the way the clathrate breaks down, serving as an indication of the strength of the non-bonded interactions in the system and the van der Waals forces between hosts and guests.

The mass spectrum, shown in Figure 3.1, was recorded on a V.G. Micromass F16 Spectrometer operating under the following conditions:

Electron beam energy	70 eV
Accelerating voltage	4 kV
Source temperature	200°C

The spectrum shows two distinct peaks. From the fragmentation patterns it is clear that dimethylsulphoxide is ionized first at a lower ion current and scan number (18), followed by predominant host breakdown at the higher ion current and scan number (35). Proposed fragmentation assignments are given in Table 3.1.

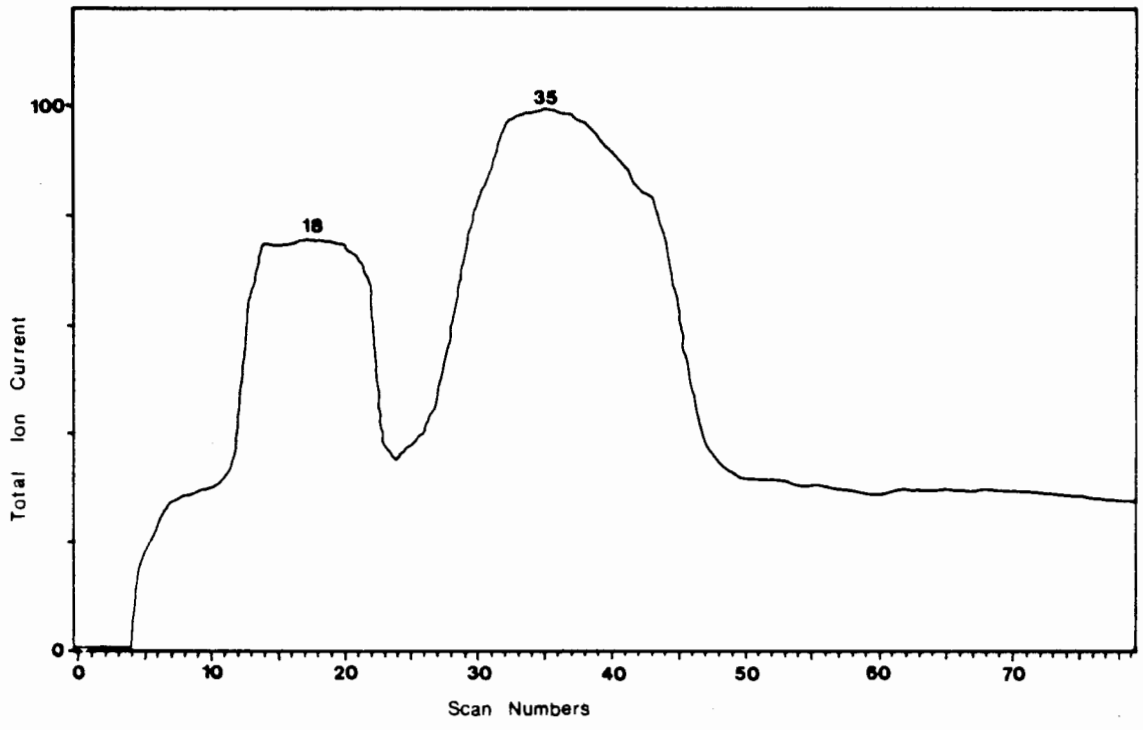


Figure 3.1 The mass spectrum of $Ni(NCS)_2(4\text{-}PhPy)_4.4DMSO$

TABLE 3.1

TOTAL ION CURRENT SPECTRUM : FRAGMENTATION PATTERNS

m/e	Relative % Abundance	Possible Inference
Scan Number 18 - Guest breakdown		
78	100	$SO(CH_3)_2^{+\cdot}$
63	100	$SO(CH_3)^+$
61	33	$SO(CH)^+/S(CH_2)_2^+$
45	42	SCH
29	17	$C_2H_5^+$
27	12	$C_2H_3^+$
Scan Number 35 - Host breakdown		
155	100	$C_{11}H_9N^{+\cdot}$
154	90	$C_{11}H_8N^+$
153	9	$C_{11}H_7N^+$
140	12	$C_{11}H_8^+$
128	33	$C_{10}H_8^+$
127	32	$C_{10}H_7^+$
126	9	$C_{10}H_6^+$
115	23	$C_9H_7^+$
102	21	$C_8H_6^+$
78	6	$C_5H_4N^+$
77	16	$C_5H_3N^+/C_6H_5^+$
76	10	$C_5H_2N^+/C_6H_4^+$
64	17	$C_5H_4^+$
63	14	$C_5H_3^+$
51	25	$C_4H_3^+$
50	13	$C_4H_2^+$

3.2 PRELIMINARY X-RAY ANALYSIS

Single crystals were selected and mounted in Lindemann capillary tubes with mother liquor due to their deterioration in air. Oscillation and zero-layer Weissenberg photographs revealed a triclinic space group with approximate cell dimensions : a = 23.02Å, b = 12.72Å, c = 9.34Å, α= 110° , β= 85°, γ= 91° and Z = 2.

3.3 INTENSITY DATA COLLECTION

A suitable single crystal cut to the required size was mounted in a Lindemann capillary tube with mother liquor. Diffractometer data collection was carried out at the C.S.I.R., Pretoria. The data set contained 8077 reflections of which 1347 were systematically absent and a further 1330 omitted since they did not satisfy the criterion $I_{rel} > 2\sigma I_{rel}$ for an observed reflection. Thus there remained 5390 reflections which constituted the "observed" data. Inspection of the data collection revealed a triclinic space group. Relevant details are listed in Table 3.2. No absorption correction factor was applied to the diffractometer data even though the A* value varied from 0.4 to 0.2. Under our circumstances, the great sensitivity of the crystals made it impossible to grind them. Consequently a high R was expected.

TABLE 3.2

CRYSTAL DATA AND REFINEMENT PARAMETERS FOR THE STRUCTURE ANALYSIS

Crystal Data

Molecular Formula	$NiC_{54}H_{60}N_6S_6O_4$
Molecular Weight	1108.2 $g.mol^{-1}$
Space Group	Triclinic, $P\bar{1}$
Z	2
a	25.21(1)Å
b	12.217(6)Å
c	10.242(5)Å
α	112.35(2)°
β	84.12(2)°
γ	90.75(2)°
V	2900.46 $Å^3$
D_m	1.24 $g.cm^{-3}$
D_c	1.27 $g.cm^{-3}$
μ(MoK α)	36.55 cm^{-1}
$\mu R_{max}, \mu R_{min}$	1.0, 0.5
A*	4.1, 2.1
F(000)	1164
Crystal dimensions	0.55 x 0.30 x 0.25 mm
Scan mode	$\omega - 2\theta$
Scan width	$0.700°\theta$
Scan speed	$0.023°\theta s^{-1}$
Range scanned	$3° < \theta < 23°$
Stability of standard reflections	1.4%
Number of reflections collected	8077
Number of "observed" reflections	5390

Final refinement

Number of variables	321
R	0.131
R_ω	0.120
Weighting scheme, ω	$(\sigma^2F + 0.000F^2)^{-1}$

4.4 SOLUTION AND REFINEMENT OF THE STRUCTURE

The space group is either P1 or $P\bar{1}$[50]. We chose the centrosymmetric $P\bar{1}$. This was in agreement with the E statistics which gave a mean abs (E x E-1) value of 0.812 for N = 1878.6, and the choice was vindicated by the correct refinement of the structure.

A three-dimensional Patterson map was computed in order to locate the nickel ion position. A vector grid for $P\bar{1}$ was simply constructed:

	x, y, z	-x, -y, -z
x, y, z -x, -y, -z	0 2x, 2y, 2z	-2x, -2y, -2z 0

giving the following Ni x Ni vectors:

Vector Position	Multiplicity
0, 0, 0	2
-2x, -2y, -2z	1
2x, 2y, 2z	1

The Ni x Ni peak was recognized at 2x = 0.4852, 2y = 0.2964 and 2z = 0.6571, this revealing the nickel coordinates at x = 0.2426, y = 0.1482 and z = 0.3285.

The model based on placing the nickel alone (R = 0.475) produced an electron density map which in the final cycle revealed the positions of twenty-eight non-hydrogen atoms of the 4-phenylpyridine (4-PhPy) rings and the isothiocyanate groups. Subsequent least-squares and accelerated full-matrix refinements lowered R to 0.308 and revealed a further twenty non-hydrogen atomic positions, three of which had to be calculated manually.

Once all the non-hydrogen atoms of the host molecule had been located, the nickel and sulphur atoms were treated anisotropically[51], reduc-

ing R to 0.270. This refinement cycle revealed four new molecular entities whose bond lengths and angles led us to suspect that we had dimethylsulphoxide (DMSO) present as guest, rather than the intended m-Xylene. Thus the ratio of host:guest was confirmed as being 1:4.

Introducing the four DMSO guest molecules into the refinement process, as well as treating all sulphur atoms anisotropically, led to the reduction of R to 0.172.

Hydrogen atoms of the host complex were introduced into the model and constrained at 1.08 $\mathring{A}$ from their respective carbon atoms. Their isotropic thermal parameters were also fixed. Hydrogen atoms of the methyl groups of the DMSO guest molecules were not included.

Thus the final least-squares refinement cycle converged to R = 0.131 and to a weighted R_ω= 0.120, where $\omega = (\sigma^2 F + 0.000F^2)^{-1}$.

The analysis of variance calculations (tabulated in Table 3.3) agreed to the refined weighting scheme. Thermal motion parameters for the host atoms were acceptably low, but those for the guest atoms ranged between 0.10 and 0.20, which is in accordance with the thermal disorder inherent to all clathrated moieties. The average shift/e.s.d. ratio for the parameters of the host was less than 0.10, indicative of satisfactory convergence.

Final atomic coordinates and their thermal motion parameters are tabulated in Table 3.4. Observed and calculated structure factors are listed in Appendix I.

TABLE 3.3

ANALYSIS OF VARIANCE

a) By parity groups

Group	*ggg*	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*	All
N	693	674	674	693	666	660	656	674	5390
V	379	383	379	370	336	372	349	366	367

b) As a function of $\sin\theta$

$\sin\theta$	0.00 - 0.17	0.17 - 0.21	0.21 - 0.24	0.24 - 0.27	0.27 - 0.29	0.29 - 0.31	0.31 - 0.34	0.34 - 0.36	0.36 - 0.38	0.38 - 0.40
N	591	530	540	646	479	453	746	591	539	275
V	629	438	421	374	341	321	252	216	194	169

c) As a function of $\sqrt{(F/F_{max})}$

$\sqrt{(F/F_{max})}$	0.00 - 0.16	0.17 - 0.17	0.18 - 0.18	0.20 - 0.20	0.21 - 0.21	0.23 - 0.23	0.26 - 0.26	0.29 - 0.29	0.34 - 0.34	1.00 - 1.00
N	836	409	403	714	349	597	622	458	465	537
V	237	275	299	314	351	359	414	453	495	449

d) As a function of |Miller index|

|h|	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	164	319	322	328	325	324	313	292	285	300	275	253	238	231	1421
V	460	449	422	471	478	416	384	392	348	384	327	319	280	290	271

|k|	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	337	659	649	633	610	551	484	436	363	290	186	123	64	5	0
V	438	461	447	407	361	319	320	294	275	238	243	238	213	225	0

|l|	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	448	760	752	685	626	573	511	406	300	212	97	20	0	0	0
V	377	435	403	348	403	337	393	306	273	177	136	114	0	0	0

N = No. of reflections in the group

V = 100 $[M\Sigma(\omega|F_o-F_c|^2)/N\Sigma\omega]$ where M = total no. of reflections

TABLE 3.4

FRACTIONAL ATOMIC COORDINATES ($\AA \times 10^4$) AND ISOTROPIC THERMAL MOTION PARAMETERS ($\AA^2 \times 10^3$) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom (Host)	x/a	y/b	z/c	U_{iso}
Ni(1)	2449(1)	1516(1)	3316(1)	a
N(1)	2012(3)	1568(7)	1759(9)	47(2)
C(1)	1690(4)	1752(8)	1153(10)	41(3)
S(1)	1216(1)	1983(3)	268(4)	a
N(2)	2907(3)	1567(7)	4914(9)	48(2)
C(2)	3269(4)	1590(9)	5535(11)	44(3)
S(2)	3785(1)	1558(3)	6328(4)	a
N(11)	3168(3)	1507(7)	2019(9)	49(2)
C(12)	3632(4)	1956(10)	2473(12)	57(3)
C(13)	4116(5)	1823(10)	1625(12)	66(4)
C(14)	4127(4)	1173(9)	159(11)	48(3)
C(15)	3628(4)	753(10)	-370(12)	58(3)
C(16)	3175(4)	921(9)	573(11)	54(3)
C(111)	4613(5)	978(10)	-856(12)	56(3)
C(112)	5046(6)	1702(13)	-411(16)	95(5)
C(113)	5526(7)	1448(14)	-1418(17)	109(5)
C(114)	5539(6)	623(13)	-2720(16)	94(5)
C(115)	5130(6)	-82(13)	-3104(15)	91(4)
C(116)	4641(5)	133(11)	-2150(13)	74(4)
N(21)	2515(3)	-373(7)	2424(8)	45(2)
C(22)	2141(5)	-1024(10)	1643(11)	57(3)
C(23)	2169(5)	-2265(10)	1044(12)	62(3)
C(24)	2596(4)	-2880(9)	1257(11)	51(3)
C(25)	2962(4)	-2187(10)	2100(11)	57(3)
C(26)	2922(4)	-976(10)	2619(11)	53(3)
C(211)	2636(4)	-4174(9)	620(11)	48(3)
C(212)	2204(5)	-4891(11)	106(12)	68(4)
C(213)	2282(6)	-6126(12)	-529(13)	79(4)
C(214)	2759(6)	-6649(13)	-685(14)	84(4)

Atom (Host)	x/a	y/b	z/c	U_{iso}
C(215)	3181(7)	-6015(14)	-180(16)	109(5)
C(216)	3116(6)	-4761(13)	482(14)	92(5)
N(31)	1732(3)	1363(7)	4536(8)	44(2)
C(32)	1250(4)	1756(9)	4420(11)	49(3)
C(33)	782(4)	1572(9)	5182(11)	52(3)
C(34)	799(4)	959(9)	6051(11)	49(3)
C(35)	1306(5)	544(10)	6174(12)	66(4)
C(36)	1753(5)	771(10)	5409(12)	62(3)
C(311)	315(4)	735(9)	6881(11)	47(3)
C(312)	-135(5)	1416(11)	7136(12)	67(4)
C(313)	-594(5)	1200(12)	7954(13)	79(4)
C(314)	-583(5)	329(11)	8422(13)	74(4)
C(315)	-144(5)	-366(12)	8186(14)	85(4)
C(316)	326(5)	-179(11)	7331(13)	80(4)
N(41)	2408(3)	3366(7)	4243(9)	48(2)
C(42)	2249(4)	3952(9)	5639(11)	50(3)
C(43)	2232(4)	5152(10)	6296(12)	55(3)
C(44)	2387(4)	5864(9)	5559(11)	47(3)
C(45)	2539(4)	5271(10)	4110(12)	57(3)
C(46)	2533(4)	4038(10)	3517(12)	57(3)
C(411)	2392(5)	7190(10)	6276(12)	59(3)
C(412)	2008(5)	7766(11)	7398(12)	67(4)
C(413)	2011(5)	9039(11)	8079(14)	78(4)
C(414)	2390(5)	9608(12)	7598(13)	75(4)
C(415)	2764(5)	9056(12)	6485(14)	83(4)
C(416)	2779(5)	7810(11)	5778(13)	73(4)
H(12)	3633(4)	2466(10)	3596(12)	b
H(13)	4473(5)	2211(10)	2087(12)	b
H(15)	3606(4)	307(10)	-1497(12)	b
H(16)	2805(4)	576(9)	152(11)	b
H(112)	5026(6)	2412(13)	622(16)	b
H(113)	5880(7)	1943(14)	-1095(17)	b
H(114)	5885(6)	528(13)	-3474(16)	b
H(115)	5162(6)	-815(13)	-4119(15)	b

Atom (Host)	x/a	y/b	z/c	U_{iso}
H(116)	4297(5)	-395(11)	-2495(13)	b
H(22)	1807(5)	-571(10)	1469(11)	b
H(23)	1860(5)	-2747(10)	418(12)	b
H(25)	3287(4)	-2607(10)	2361(11)	b
H(26)	3235(4)	-478(10)	3214(11)	b
H(212)	1814(5)	-4496(11)	198(12)	b
H(213)	1946(6)	-6671(12)	-899(13)	b
H(214)	2805(6)	-7598(13)	-1228(14)	b
H(215)	3563(7)	-6443(14)	-276(16)	b
H(216)	3456(6)	-4247(13)	898(14)	b
H(32)	1221(4)	2230(9)	3728(11)	b
H(33)	403(4)	1915(9)	5073(11)	b
H(35)	1345(5)	61(10)	6852(12)	b
H(36)	2138(5)	457(10)	5519(12)	b
H(312)	-149(5)	2109(11)	6728(12)	b
H(313)	-949(5)	1756(12)	8194(13)	b
H(314)	-937(5)	168(11)	9004(13)	b
H(315)	-137(5)	-1044(12)	8621(14)	b
H(316)	674(5)	-759(11)	7061(13)	b
H(42)	2128(4)	3437(9)	6267(11)	b
H(43)	2095(4)	5556(10)	7413(12)	b
H(45)	2659(4)	5763(10)	3454(12)	b
H(46)	2638(4)	3605(10)	2385(12)	b
H(412)	1711(5)	7269(11)	7757(12)	b
H(413)	1716(5)	9515(11)	8948(14)	b
H(414)	2400(5)	10559(12)	8124(13)	b
H(415)	3052(5)	9578(12)	6139(14)	b
H(416)	3075(5)	7361(11)	4898(13)	b

Atom (Guests)	x/a	y/b	z/c	U_{iso}
Guest Molecule 1				
S(30)	9308(2)	4246(5)	855(9)	a
O(30)	8808(5)	3683(10)	755(12)	138(4)
C(301)	9252(8)	5696(17)	1911(20)	150(7)
C(302)	9800(7)	3570(17)	1417(20)	146(7)

Atom (Guests)	x/a	y/b	z/c	U_{iso}
Guest Molecule 2				
S(40)	5665(3)	4186(7)	6851(9)	a
O(40)	6119(5)	3464(12)	6596(14)	174(5)
C(401)	5497(13)	4840(28)	8573(34)	282(14)
C(402)	5159(9)	3221(20)	6091(23)	178(9)
Guest Molecule 3				
S(50)	9250(2)	3782(5)	5409(7)	a
O(50)	9761(5)	3725(12)	5856(14)	167(5)
C(501)	9041(7)	5287(16)	6078(19)	141(7)
C(502)	8744(8)	3161(19)	6217(22)	174(8)
Guest Molecule 4				
S(60)	4001(3)	6088(5)	7911(9)	a
O(60)	4466(6)	6181(14)	7252(16)	209(6)
C(601)	3671(8)	4937(18)	6562(22)	170(8)
C(602)	3596(8)	7324(18)	8056(22)	166(8)

a Anisotropic thermal parameters of the form:
$T = \exp [-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2\ U_{23}\ klb^*c^* + 2\ U_{13}hla^*c^* + 2\ U_{12}hka^*b^*) \times 10^3]$

with parameters

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni(1)	42(1)	38(1)	38(1)	6(1)	-1(1)	0(1)
S(1)	58(2)	90(3)	92(3)	48(2)	-19(2)	-3(2)
S(2)	52(2)	99(3)	70(2)	26(2)	-17(2)	-2(2)
S(30)	124(5)	104(4)	404(11)	51(5)	-110(6)	-16(4)
S(40)	147(6)	250(9)	264(9)	5(7)	-68(6)	27(6)
S(50)	143(5)	142(5)	214(6)	82(4)	-30(4)	5(4)
S(60)	185(6)	123(5)	290(9)	50(5)	-79(6)	-22(4)

b All H atoms have U_{iso} = 114(13)

3.5. DESCRIPTION OF THE CLATHRATE STRUCTURE

(i) MOLECULAR STRUCTURE

Host Molecule

Intramolecular bond lengths and angles of the host and guest molecules, with estimated standard deviations, are given in Tables 3.5 and 3.6 respectively. Least-squares planes through various groups of atoms and selected torsion angles are presented in Table 3.7.

The host molecule $Ni(NCS)2(4\text{-}PhPy)_4$ adopts distorted octahedral conformation, the nickel atom being coordinated to two isothiocyanate groups and four 4-phenylpyridine ligands. The overall shape of the molecule is depicted in Figure 3.2. The nickel atom is positioned directly in the molecular plane defined by the atoms N(11), N(21), N(31) and N(41), with only slight deviation from planarity of 0.02Å. Angles subtended by the nickel atom in this plane vary from 87.1(9)°to 92.5(9)°. See diagram in Figure 3.3.

The average Ni-N bond length for the pyridine ligands is 2.124(10)Å whereas that for the isothiocyanate ligands is 2.064(8)Å, a significant difference (more than six times their standard deviation). This lengthening of the Ni-N distance of the pyridine ligands is caused by intramolecular repulsion between the isothiocyanate and pyridine ligands.

The angles subtended at the nickel atom from N(1) and N(2) of the isothiocyanate ligands to the plane defined by the N atoms of the pyridine ligands deviate from 90°, since the angle N(1) - Ni(1) - N(2) is 176.5(9)°. Torsion angles C(1) - N(1) - Ni(1) - N(21) and C(2) - N(2) - Ni(1) - N(21) are 127.2(9)° and 86.6(9)° respectively, indicating that the conformation of the isothiocyanate groups about the Ni-N bonds is asymmetric.

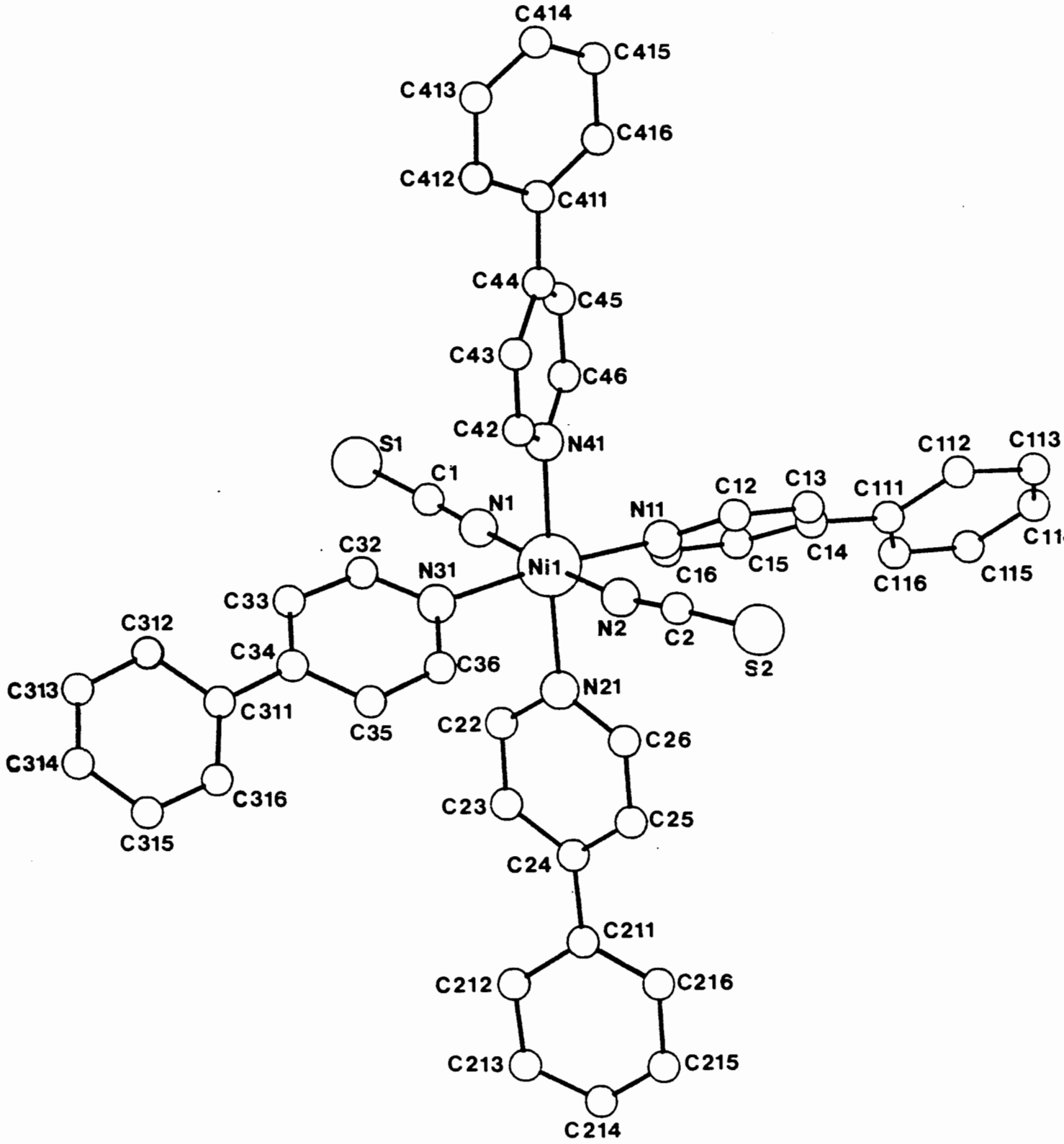


Figure 3.2 The Host Complex $Ni(NCS)_2(4\text{-}PhPy)_4$

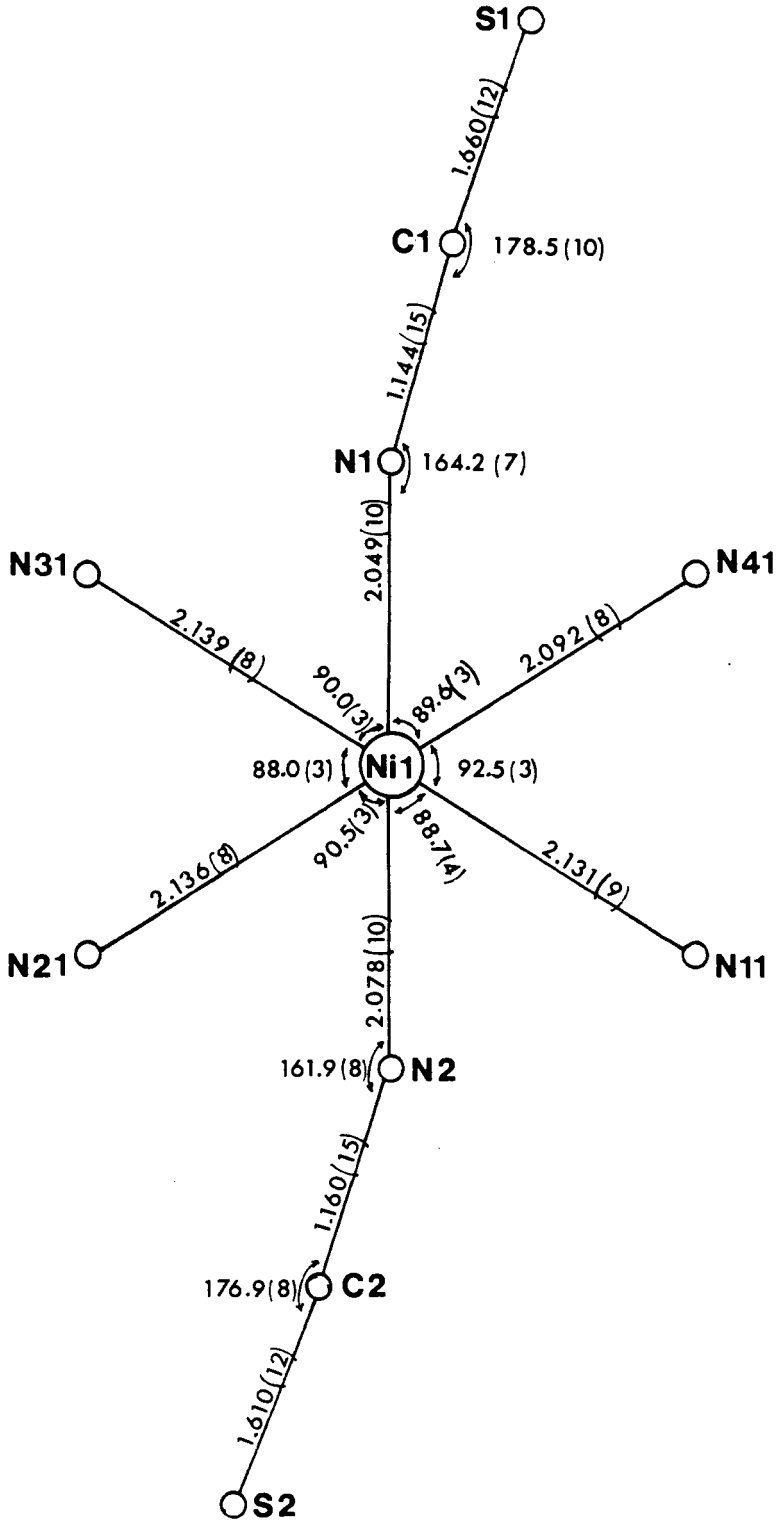


Figure 3.3 The Environment of the Nickel Atom, indicating bond lengths (Å) and angles (°)

The isothiocyanate ligands themselves are not linear, as has been observed in all previous study of such structures. The signifcant deviation from linearity is obvious at N(1) and N(2), the angles being 161.9(9)° and 164.2(9)° respectively, whereas the angles at C(1) and C(2) are 178.5(9)° and 176.9(9)° respectively. It has been suggested[52] that the differences in the Ni-N-C(S) bond angles in different crystal structures cannot be ascribed to any electronic effect, but should rather be interpreted in terms of the specific molecular packing. Permissible Ni-N-C(S) bond angles range from 150° to 180°.

Least-squares planes through all the pyridine and phenyl rings indicate that the rings are essentially planar, the maximum deviation in either plane being only 0.03Å.

All pyridine and phenyl rings are twisted with respect to the N(11) - N(21) - N(31) - N(41) plane.

The twist of the bond between individual pyridine rings and the nickel plane may be expressed more specifically in terms of torsion angles, which have been listed in Table 3.7. The rings are twisted at angles of 58.2(9)° for pyridine ring 1, 62.8(9)° for pyridine ring 2, 64.1(9)° for pyridine ring 3, and suddenly there is a vast change to 39.3(9)° for pyridine ring 4. Angles between normals to the planes confirm this trend.

This difference in torsion angle was also observed when considering the twists between the pyridine and phenyl rings within each ligand. Torsion angles display twists of 21.4(9)° within ligand 1, 19.0(9)° within ligland 2, 22.9(9)° within ligand 3, while the pyridine-phenyl twist of ligand 4 is 33.9(9)°.

The pyridine ligands in *trans* positions are also twisted with respect to each other. The angle between the N(11) and N(31) moieties is 62.2(9)°, while that between the N(21) and N(41) moeities is 102.7(9)°.

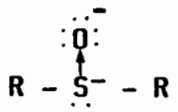
Thus the ligands coordinated to the nickel atom orientate themselves at suitable angles such that minimal steric interaction takes place between the groups. The aim is to create a stable environment to enable the guest to fit comfortably into the cavities formed by the flexible conformation of the ligands. A potential energy investigation of the clathrate systems demonstrating this versatility in host conformation, is discussed further in Chapter 6.

It is of interest to note that the thermal motion parameters of the phenyl groups are higher than those of the pyridine groups; the phenyl groups possess greater vibrational freedom owing to their larger distance from the nickel atom, accommodating the flexibility in conformation required to form a cavity.

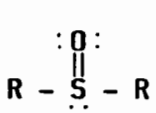
Guest Molecules

The bond lengths and angles of the four DMSO guest molecules vary from one another. On average the S-O distance is 1.39(2)Å and the S-C distance 1.75(2)Å.

Reported values for the S-O distance are 1.531(5)Å[53] and 1.47(4)Å from electron diffraction studies[54, 55]. A long-standing controversy exists regarding the proper description of the S-O bond. The difference in viewpoint lies in whether the semi-polar (A) or the doubly covalent structure (B) is the major contribution to the resonance hybrid.



(A)



(B)

Cruickshank[56] concludes that S-O bond shortenings can be explained solely on the basis of 2p-3d-π - bonding. There is also the proposition by Sass, Vidale and Donohue[57], and Caron, Palenick, Goldish and Donohue[58] that increasing opposite charges across a bond have a shortening effect on the bond length.

Reported values for S-C bond lengths are 1.798(10)Å[53] and 1.78(1)Å for the trimethyloxosulphonium ion[59, 60], not significantly different to our average value of 1.75(2)Å. Electron diffraction values of 1.82 - 1.84Å are somewhat higher. As expected this is essentially a normal covalent single bond.

There seems to be no explanation as to why the two S-C distances which are chemically equivalent are found to be different by as much as 0.109Å in Guest Molecule 2.

Reported values by Thomas *et al* for the O-S-C and C-S-C angles are 106.8(4)° and 97.4(4)°, while electron diffraction values are 106(6)° and 100(5)° respectively. These compare well with our found valuies for Guest Molecules 2,3 and 4. Values for Guest Molecule 1 are somewhat greater.

Figure 3.4 is a diagramatic representation of the DMSO molecule with mean bond lengths and angles. Bond lengths are the mean lengths of molecules 1, 2, 3 and 4, while angles are the means of molecules 2, 3 and 4 only.

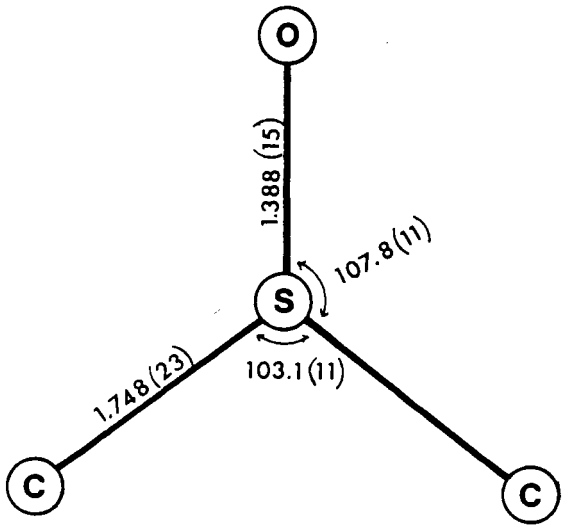


Figure 3.4

TABLE 3.5

BOND LENGTHS (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Host Molecule

Ni(1) - N(1)	2.049(10)
Ni(1) - N(2)	2.078(10)
Ni(1) - N(11)	2.131(9)
Ni(1) - N(21)	2.136(8)
Ni(1) - N(31)	2.139(8)
Ni(1) - N(41)	2.092(8)
N(1) - C(1)	1.144(15)
N(2) - C(2)	1.160(15)
C(1) - S(1)	1.660(12)
C(2) - S(2)	1.610(12)
N(11) - C(12)	1.336(14)
C(12) - C(13)	1.395(16)
C(13) - C(14)	1.405(15)
C(14) - C(15)	1.431(16)
C(15) - C(16)	1.383(15)
N(11) - C(16)	1.377(13)
C(14) - C(111)	1.482(15)
C(111) - C(112)	1.396(18)
C(112) - C(113)	1.462(21)
C(113) - C(114)	1.329(19)
C(114) - C(115)	1.326(21)
C(115) - C(116)	1.454(19)
C(111) - C(116)	1.330(15)
N(21) - C(22)	1.346(13)
N(21) - C(26)	1.345(15)
C(22) - C(23)	1.402(16)
C(23) - C(24)	1.402(18)
C(24) - C(25)	1.379(15)
C(25) - C(26)	1.370(16)
C(211) - C(212)	1.405(16)
C(24) - C(211)	1.463(14)

Host Molecule

C(211) - C(216)	1.381(19)
C(212) - C(213)	1.405(18)
C(213) - C(214)	1.335(20)
C(214) - C(215)	1.336(21)
C(215) - C(216)	1.423(21)
N(31) - C(32)	1.344(14)
N(31) - C(36)	1.352(17)
C(32) - C(33)	1.412(16)
C(33) - C(34)	1.368(19)
C(34) - C(35)	1.416(17)
C(34) - C(311)	1.498(16)
C(35) - C(36)	1.390(18)
C(311) - C(312)	1.359(16)
C(311) - C(316)	1.363(20)
C(312) - C(313)	1.438(18)
C(313) - C(314)	1.324(23)
C(314) - C(315)	1.348(20)
C(315) - C(316)	1.467(20)
N(41) - C(42)	1.352(12)
N(41) - C(46)	1.318(17)
C(42) - C(43)	1.360(15)
C(43) - C(44)	1.382(19)
C(44) - C(45)	1.395(14)
C(44) - C(411)	1.503(15)
C(45) - C(46)	1.393(15)
C(411) - C(412)	1.389(15)
C(411) - C(416)	1.399(19)
C(412) - C(413)	1.442(17)
C(413) - C(414)	1.336(20)
C(414) - C(415)	1.361(17)
C(415) - C(416)	1.415(18)

Guest Molecule 1

S(30) - O(30)	1.422(13)
S(30) - C(301)	1.687(18)
S(30) - C(302)	1.756(23)

Guest Molecule 2

S(40) - O(40)	1.396(16)
S(40) - C(401)	1.647(31)
S(40) - C(402)	1.756(23)

Guest Molecule 3

S(50) - O(50)	1.420(15)
S(50) - C(501)	1.766(19)
S(50) - C(502)	1.769(24)

Guest Molecule 4

S(60) - O(60)	1.316(17)
S(60) - C(601)	1.819(20)
S(60) - C(602)	1.785(24)

All C - H bond lengths	1.080(18)

TABLE 3.6

BOND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Host Molecule

N(2) - Ni(1) - N(1)	176.5(4)
N(11) - Ni(1) - N(1)	90.0(4)
N(11) - Ni(1) - N(2)	88.7(4)
N(21) - Ni(1) - N(1)	92.7(3)
N(21) - Ni(1) - N(2)	90.5(3)
N(21) - Ni(1) - N(11)	87.1(3)
N(31) - Ni(1) - N(1)	90.0(3)
N(31) - Ni(1) - N(2)	91.5(3)
N(31) - Ni(1) - N(11)	175.1(3)
N(31) - Ni(1) - N(21)	88.0(3)
N(41) - Ni(1) - N(1)	89.6(3)
N(41) - Ni(1) - N(2)	87.2(3)
N(41) - Ni(1) - N(11)	92.5(3)
N(41) - Ni(1) - N(21)	177.7(4)
N(41) - Ni(1) - N(31)	92.4(3)
C(1) - N(1) - Ni(1)	164.2(7)
C(2) - N(2) - Ni(1)	161.9(8)
N(1) - C(1) - S(1)	178.5(10)
N(2) - C(2) - S(2)	176.9(8)
C(12) - N(11) - Ni(1)	126.4(7)
C(16) - N(11) - Ni(1)	118.0(7)
C(16) - N(11) - C(12)	115.5(9)
C(13) - C(12) - N(11)	125.8(10)
C(14) - C(13) - C(12)	118.5(11)
C(15) - C(14) - C(13)	116.8(10)
C(111) - C(14) - C(13)	123.7(10)
C(111) - C(14) - C(15)	119.3(9)
C(16) - C(15) - C(14)	119.5(10)
C(15) - C(16) - N(11)	123.6(10)
C(112) - C(111) - C(14)	118.0(9)
C(116) - C(111) - C(14)	121.2(11)

Host Molecule

C(116) - C(111) - C(112)	120.7(11)
C(113) - C(112) - C(111)	116.4(11)
C(114) - C(113) - C(112)	121.7(14)
C(115) - C(114) - C(113)	120.7(15)
C(116) - C(115) - C(114)	119.7(11)
C(115) - C(116) - C(111)	120.4(12)
C(22) - N(21) - Ni(1)	121.0(8)
C(26) - N(21) - Ni(1)	122.5(6)
C(26) - N(21) - C(22)	116.4(9)
C(23) - C(22) - N(21)	122.8(11)
C(24) - C(23) - C(22)	120.1(10)
C(25) - C(24) - C(23)	115.6(10)
C(211) - C(24) - C(23)	120.9(10)
C(211) - C(24) - C(25)	123.5(11)
C(26) - C(25) - C(24)	121.5(11)
C(25) - C(26) - N(21)	123.5(10)
C(212) - C(211) - C(24)	123.3(10)
C(216) - C(211) - C(24)	120.6(10)
C(216) - C(211) - C(212)	116.0(10)
C(213) - C(212) - C(211)	119.5(12)
C(214) - C(213) - C(212)	122.1(13)
C(215) - C(214) - C(213)	120.9(14)
C(216) - C(215) - C(214)	118.5(15)
C(215) - C(216) - C(211)	122.8(13)
C(32) - N(31) - Ni(1)	123.7(8)
C(36) - N(31) - Ni(1)	118.6(7)
C(36) - N(31) - C(32)	117.5(9)
C(33) - C(32) - N(31)	121.8(12)
C(34) - C(33) - C(32)	121.0(11)
C(35) - C(34) - C(33)	117.2(11)
C(311) - C(34) - C(33)	123.2(10)
C(311) - C(34) - C(35)	119.6(12)
C(36) - C(35) - C(34)	118.8(13)
C(35) - C(36) - N(31)	123.7(12)

Host Molecule

C(312) - C(311) - C(34)	120.0(12)
C(316) - C(311) - C(34)	119.3(10)
C(316) - C(311) - C(312)	120.7(11)
C(313) - C(312) - C(311)	119.1(13)
C(314) - C(313) - C(312)	120.5(12)
C(315) - C(314) - C(313)	122.0(13)
C(316) - C(315) - C(314)	118.5(15)
C(315) - C(316) - C(311)	119.0(12)
C(42) - N(41) - Ni(1)	121.8(8)
C(46) - N(41) - Ni(1)	122.7(6)
C(46) - N(41) - C(42)	115.6(9)
C(43) - C(42) - N(41)	123.8(12)
C(44) - C(43) - C(42)	121.2(10)
C(45) - C(44) - C(43)	115.6(10)
C(411) - C(44) - C(43)	122.0(9)
C(411) - C(44) - C(45)	122.4(11)
C(46) - C(45) - C(44)	119.5(12)
C(45) - C(46) - N(41)	124.3(10)
C(412) - C(411) - C(44)	119.1(11)
C(416) - C(411) - C(44)	119.0(9)
C(416) - C(411) - C(412)	121.8(11)
C(413) - C(412) - C(411)	119.1(12)
C(414) - C(413) - C(412)	117.8(11)
C(415) - C(414) - C(413)	123.7(12)
C(416) - C(415) - C(414)	120.9(14)
C(415) - C(416) - C(411)	116.6(10)

Guest Molecule 1

O(30) - S(30) - C(301)	112.3(8)
O(30) - S(30) - C(302)	114.3(10)
C(301) - S(30) - C(302)	109.0(10)

Guest Molecule 2

O(40) - S(40) - C(401)	109.8(15)
O(40) - S(40) - C(402)	105.3(10)
C(401) - S(40) - C(402)	108.9(14)

Guest Molecule 3

O(50) - S(50) - C(501)	107.7(9)
O(50) - S(50) - C(502)	113.3(11)
C(501) - S(50) - C(502)	101.9(10)

Guest Molecule 4

O(60) - S(60) - C(601)	104.2(10)
O(60) - S(60) - C(602)	106.8(12)
C(601) - S(60) - C(602)	98.4(10)

TABLE 3.7

LEAST-SQUARES PLANES AND TORSION ANGLES

1(a) Equations of Least-Squares Planes Expressed in Orthogonalised Space as $pX + qY + rZ = S$

Plane 1: The pyridine ring atoms [N(11), C(12), C(13), C(14), C(15), C(16)]

$-5.6784\ X + 11.8619\ Y - 5.0294\ Z = -1.0027$

Plane 2: The phenyl ring atoms [C(111), C(112), C(113), C(114), C(115), C(116)]

$9.9308\ X - 10.3954\ Y + 7.0842\ Z = 2.9568$

Plane 3: The pyridine ring atoms [N(21), C(22), C(23), C(24), C(25), C(26)]

$-10.9168\ X - 4.3724\ Y + 8.7254\ Z = -0.4651$

Plane 4: The phenyl ring atoms [C(211), C(212), C(213), C(214), C(215), C(216)]

$-3.2626\ X - 5.3890\ Y + 9.9401\ Z = 2.0189$

Plane 5: The pyridine ring atoms [N(31), C(32), C(33), C(34), C(35), C(36)]

$4.9561\ X + 7.4708\ Y + 5.0231\ Z = 4.1567$

Plane 6: The phenyl ring atoms [C(311), C(312), C(313), C(314), C(315), C(316)]

$10.5959\ X + 4.0116\ Y + 7.0931\ Z = 5.4931$

Plane 7: The pyridine ring atoms [N(41), C(42), C(43), C(44), C(45), C(46)]

$24.5564\ X - 1.5486\ Y + 3.2968\ Z = 6.7722$

Plane 8: The phenyl ring atoms [C(411), C(412), C(413), C(414), C(415), C(416)]

$17.2554\ X - 4.4010\ Y + 8.0983\ Z = 6.0400$

Plane 9: The molecular plane defined by atoms [N(11), N(21), N(31), N(41)]

15.5607 X - 3.7729 Y + 8.6628 Z = 6.1318

1(b) Deviations of Selected Atoms from the Planes ($\mathring{A} \times 10^3$) with $\sigma \times 10^3 < 20$

Atom	Plane 1
Ni(1)	-257
N(11)*	-24
C(12)*	17
C(13)*	11
C(14)*	-29
C(15)*	22
C(16)*	4
C(111)	-26
N(21)	-2087
N(31)	-645
N(41)	1494

Atom	Plane 2
Ni(1)	248
N(11)	53
C(14)	35
C(111)*	1
C(112)*	-6
C(113)*	21
C(114)*	-31
C(115)*	24
C(116)*	-9
N(21)	1646
N(31)	560
N(41)	-1059

Atom	Plane 3
Ni(1)	22
N(11)	-1891
N(21)*	-2
C(22)*	9
C(23)*	-1
C(24)*	-13
C(25)*	20
C(26)*	-13
C(211)	-46
N(31)	1936
N(41)	67

Atom	Plane 4
Ni(1)	-339
N(11)	-1858
N(21)	-229
C(24)	-64
C(211)*	-13
C(212)*	3
C(213)*	12
C(214)*	-17
C(215)*	6
C(216)*	9
N(31)	1190
N(41)	-401

Atom	Plane 5
Ni(1)	-145
N(11)	-447
N(21)	-1971
N(31)*	-2
C(32)*	-5
C(33)*	8
C(34)*	-5
C(35)*	-2
C(36)*	5
C(311)	5
N(41)	1683

Atom	Plane 6
Ni(1)	62
N(11)	-100
N(21)	-1258
N(31)	106
C(34)	30
C(311)*	16
C(312)*	-6
C(313)*	1
C(314)*	-5
C(315)*	14
C(316)*	-20
N(41)	1418

Atom	Plane 7
Ni(1)	100
N(11)	1440
N(21)	261
N(31)	-1235
N(41)*	18
C(42)*	-2
C(43)*	-13
C(44)*	14
C(45)*	1
C(46)*	-18
C(411)	57

Atom	Plane 8
Ni(1)	204
N(11)	398
N(21)	427
N(31)	22
N(41)	70
C(44)	0
C(411)*	6
C(412)*	-2
C(413)*	-5
C(414)*	9
C(415)*	-4
C(416)*	-3

* Atoms used to calculate the least-squares plane.

1(c) Angles between Normals to Planes (°)

Plane 1 and 2	161.3
" 1 " 3	110.2
" 1 " 4	119.8
" 1 " 5	62.2
" 1 " 6	82.2
" 1 " 7	110.6
" 1 " 8	124.4
" 1 " 9	120.7
Plane 2 and 3	64.3
" 2 " 4	50.0
" 2 " 5	99.6
" 2 " 6	79.2
" 2 " 7	56.6
" 2 " 8	37.2
" 2 " 9	40.6
Plane 3 and 4	18.4
" 3 " 5	71.2
" 3 " 6	66.9
" 3 " 7	102.7
" 3 " 8	69.0
" 3 " 9	63.8
Plane 4 and 5	67.6
" 4 " 6	56.9
" 4 " 7	84.4
" 4 " 8	50.7
" 4 " 9	45.7
Plane 5 and 6	21.2
" 5 " 7	74.3
" 5 " 8	66.0
" 5 " 9	60.5
Plane 6 and 7	57.6
" 6 " 8	44.8
" 6 " 9	39.4
Plane 7 and 8	33.8
" 7 " 9	39.0
Plane 8 and 9	7.0

2. Selected Torsion Angles (°)

C(16) - N(11) - Ni(1) - N(21)	58.2
C(22) - N(21) - Ni(1) - N(31)	62.8
C(32) - N(31) - Ni(1) - N(41)	64.3
C(46) - N(41) - Ni(1) - N(11)	39.3
C(116) - C(111) - C(14) - C(15)	-21.4
C(216) - C(211) - C(24) - C(25)	-19.0
C(316) - C(311) - C(34) - C(35	-22.9
C(412) - C(411) C(44) - C(43)	-33.9

(ii) MOLECULAR PACKING

The clathrating framework is formed by molecular units of $Ni(NCS)_2(4\text{-}PhPy)_4$ molecules whose orientation determine the cavities in which the guest molecules are housed.

Figure 3.5 depicts a visual projection down the Z axis showing one unit cell comprising its two host and eight guest molecules. Figure 3.6 shows a perspective view of the unit cell.

Figure 3.7 represents a view down the Z axis, showing how the host molecules stack to form two distinct voids. Call them Channels I and II.

Each channel is almost rhomboidal in cross-section and is surrounded by four 4-phenylpyridine ligands forming the "walls" around the tunnels that run through the lattice parallel to the Z axis.

Figures 3.8 and 3.9 depict the molecular packing viewed down the Y axis. The NCS groups of the host molecule are shown to constrict the channels.

In Channel I the 4-phenylpyridine planes are virtually parallel to the tunnel. The pyridine ring of ligand 4 is also almost parallel to the tunnel - this explains why the twisting about the Ni-N(41) bond is so exaggerated.

The phenyl and pyridine rings constituting the walls of Channel II are not planar with respect to each other and to the general direction of the channel, thus making the environment along Channel II more corrugated.

There is no π-bonding electronic interaction between the aromatic rings since the distance between the planes is too great ($>4\mathring{A}$) and most of the planes lie at an angle to each other.

The large twisting of the torsion angles of ligand 4 compared to the other ligands indicates the flexibility of the conformation of the host molecules.

The shape of the channels is depicted more clearly in Chapter 6, in the discussion of the potential energy environment of the crystal lattice.

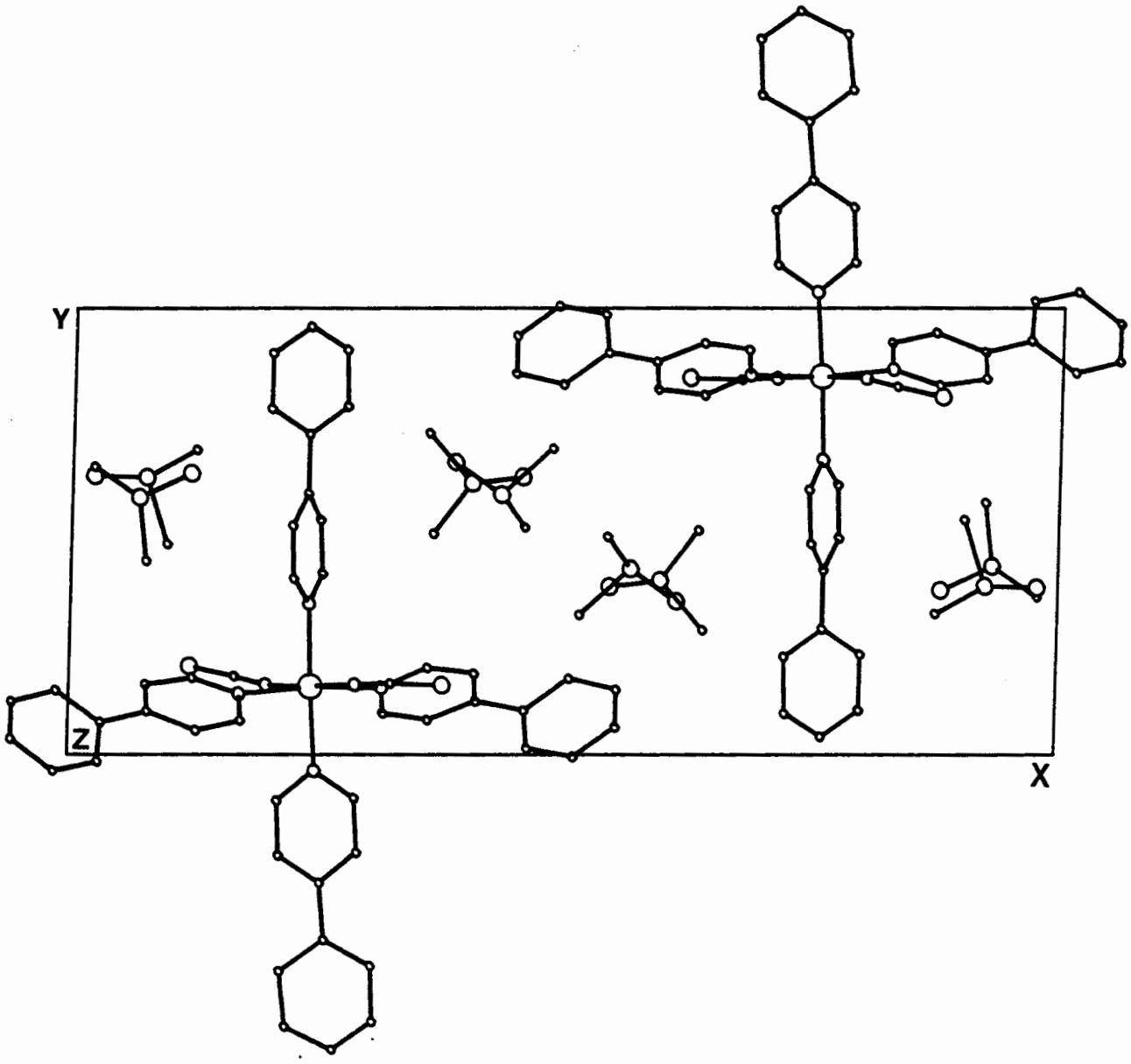


Figure 3.5 One Unit Cell viewed down the Z axis

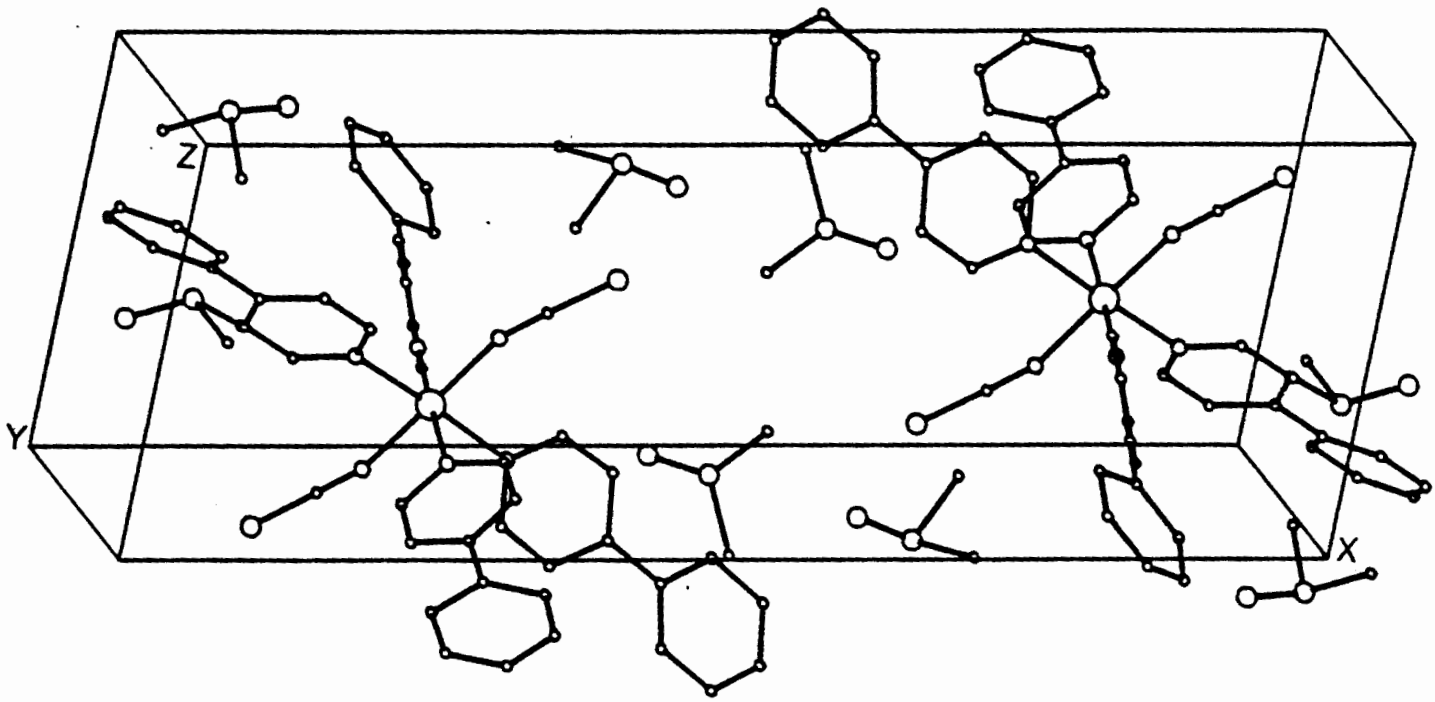


Figure 3.6 A Perspective View of one Unit Cell

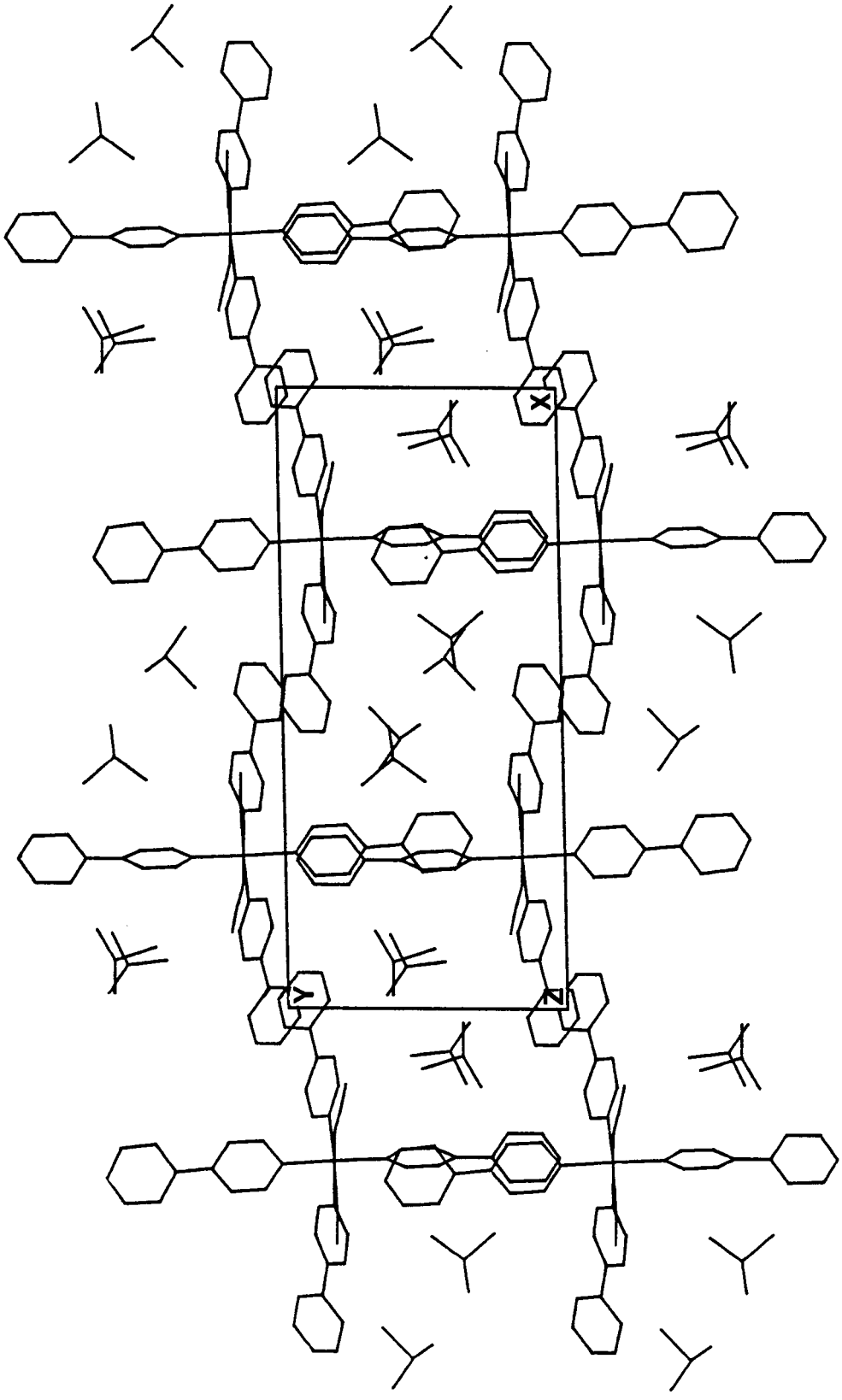


Figure 3.7 The Molecular Packing of the Clathrate $Ni(NCS)_2(4\text{-}PhPy)_4$. 4DMSO showing Channels I and II

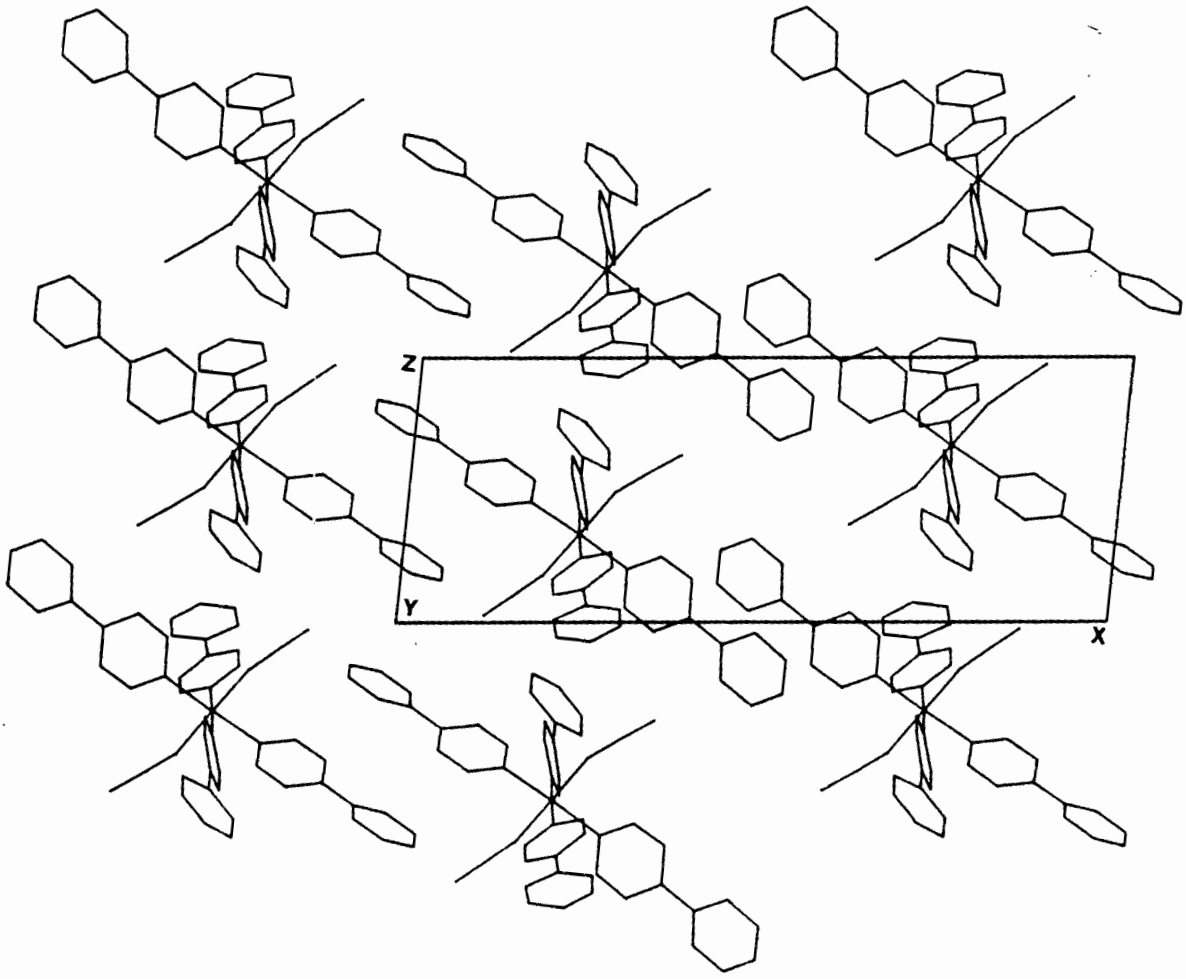


Figure 3.8 The Molecular Packing of the Host Molecules viewed down the Y axis

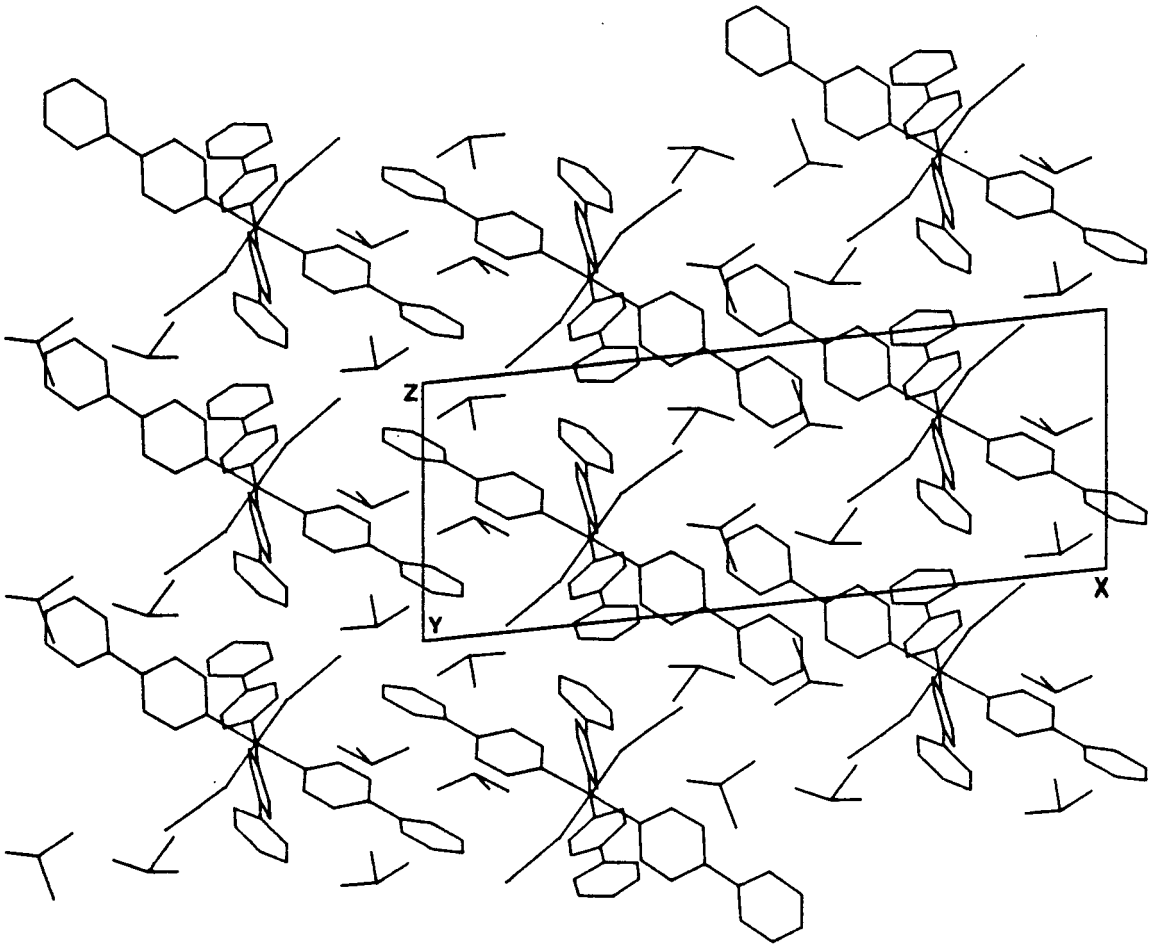


Figure 3.9 Molecular Packing including the DMSO Guest Molecules, viewed down the Y axis

CHAPTER 4

CHAPTER 4

THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(ISOTHIOCYANATO)TETRA (3-METHYLPYRIDINE)NICKEL(II).CHLOROFORM

4.1 SYNTHESIS AND CHEMICAL CHARACTERIZATION

Synthesis

The host complex $Ni(NCS)_2(3\text{-methylpyridine})_4$ was synthesized according to the method described in Chapter 2. Its purity was checked by complexiometric titration to determine nickel content.

The clathrate crystals were formed as follows:

0.80g (0.00146 mol) of $Ni(NCS)_2(3\text{-methylpyridine})_4$ was dissolved in 30 ml chloroform and heated to boiling point. Two drops of 3-methylpyridine (3-MePy) were added as excess to produce a clear violet-blue solution. To this solution was added 2.0 ml (0.01608 mol) of hot p-Xylene. This was sealed and allowed to stand under normal atmospheric conditions. Deep-blue, rather irregularly-shaped octahedral crystals of $Ni(NCS)_2(3\text{-MePy})_4$-chloroform crystallized within five days. These were kept under mother liquor to prevent their fast deterioration in air.

Analyses

Microanalysis

Elemental analysis was carried out on the clathrate crystals to determine their percentage content of carbon, hydrogen and nitrogen. If no guest had been "trapped" in our clathrate, we would have expected the theoretical percentages for pure $Ni(NCS)_2(3\text{-MePy})_4$, that is, 57.0%C, 5.2%H and 15.4%N.

Had the intended guest been clathrated, we would have expected: 62.48%C, 5.86%H and 12.86%N

However, the results obtained were:

	%C	%H	%N
Sample 1	48.70	4.40	12.70
Sample 2	48.70	4.45	12.70
Sample 3	48.70	4.35	12.65

These results led to the assumption that some other guest species was present, perhaps in addition to the p-Xylene. Supported by other chemical investigations, the results corresponded well with theoretically calculated percentages for the clathrate $Ni(NCS)_2(3\text{-}MePy)_4$. chloroform, chloroform being the solvent used, i.e. 48.60%C, 4.30%H and 12.60%N.

We can thus safely assume that there is no p-Xylene present, and that the ratio of host complex to guest species, namely chloroform, is 1:1.

Density Measurements

The density of the clathrate crystals was determined by the flotation method using potassium iodide (ρ = 1.63 $g.cm^{-3}$) and water. A mean density of D_m = 1.31 $g.cm^{-3}$ was evaluated. Using the crystallographic deduction that there are sixteen molecules per unit cell, the number of guest molecules were determined from the formula:

$$Z_h\ (M_h) + Z_g(M_g) = ND_m abc\mathcal{K} \times 10^{-24}$$

where Z_h = 16, the number of host molecules per unit cell,
M_h = 547.39 $g.mol^{-1}$, the molecular weight of the host,
M_g = 119.37 $g.mol^{-1}$, the molecular weight of the guest,
N = Avogadro constant,
D_m = 1.31 $g.cm^{-3}$, the measured density, and
$abc\mathcal{K}$ = 13736.59 $Å^3$, the volume of the unit cell.
($\mathcal{K}$ = 1 for an orthorhombic cell)

Thus Z_g, the number of guest molecules in the unit cell, is calculated to be 17.43, giving a host to guest ratio of 1:1.09, from which we may confirm with safety that there is one chloroform molecule present per host molecule.

The calculated density, D_c, using Z_g = 16, was found to be 1.29 $g.cm^{-3}$.

Mass Spectroscopy

The mass spectrum confirmed the presence of chloroform as guest inside the clathrate structure and gave an indication of the rapidity with which it breaks down. The spectrum was recorded on a V.G. Micromass F16 Spectrometer operating under the following conditions:

Electron beam energy	70 eV
Accelerating voltage	2 kV
Source temperature	175°C

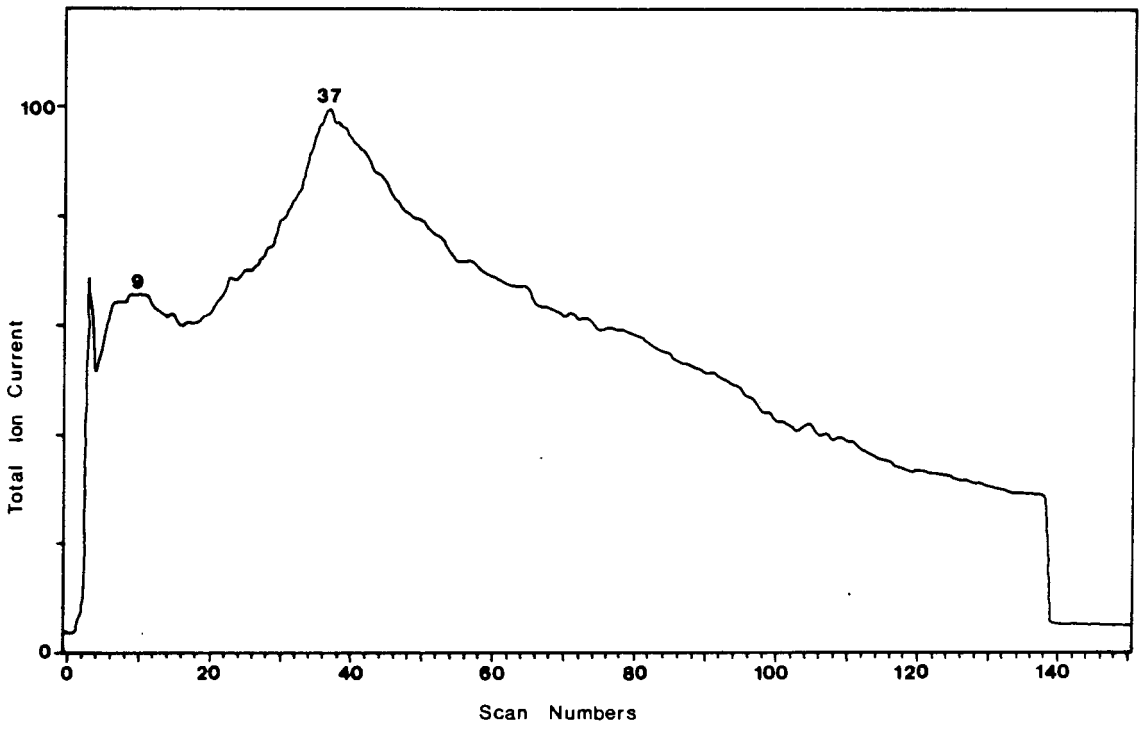


Figure 4.1 The Mass Spectrum of $Ni(NCS)_2(3\text{-}MePy)_4.CHCl_3$

The total ion current spectrum, shown in Figure 4.1, shows a small peak at scan number 9 attached to the large peak at scan number 37. The analysis of the fragmentation pattern at the low scan number, presented in Table 4.1, indicates that the initial ionization is rapid and involves breakdown of the guest, chloroform. It is of interest to note that in the region between the scan numbers 9 and 37, the relative abundance of the chloroform ion peaks diminish rapidly, such that by scan number 37 there is no guest species present whatsoever. This confirms the volatility of chloroform and suggests that in this study the intermolecular forces holding the guest in the host lattice can be overcome. The fragmentation pattern at the high scan number, presented in the same Table, shows no chloroform ions, only the ready fragmentation of the 3-methylpyridine ligands.

A sharp peak was observed at the start of the spectrum, whose fragmentation pattern was related to p-Xylene breakdown, and which did not appear again at any stage during the ionization process. This was indicative of some p-Xylene from the mother liquor on the surface of the crystal.

TABLE 4.1

TOTAL ION CURRENT SPECTRUM : FRAGMENTATION PATTERNS

m/e	Relative % Abundance	Possible Inference
Scan Number 9 - Guest breakdown		
47.5	38	CCl^+
48.5	18	$CHCl^+$
83	100	CCl_2^+
85	65	$CH_2Cl_2^+$
120	2	$CHCl_3^{+\cdot}$
Scan Number 37 - Host breakdown		
28	100	N_2^+
37	27	C_3H^+
38	63	$C_3H_2^+$
39	100	$C_3H_3^+$
50	24	$C_4H_2^+$
51	50	$C_4H_3^+$
52	26	$C_4H_4^{+\cdot}$
65	100	$C_5H_5^+$
66	100	$C_5H_6^+$
78	35	$C_5H_4N^+$
92	100	$C_7H_6N^+$
93	100	$C_7H_7N^{+\cdot}$

Quantitative Nuclear Magnetic Resonance Spectroscopy

The ^1H N.M.R. spectrum of $Ni(NCS)_2(3\text{-}MePy)_4.CHCl_3$, taken in $CDCl_3$, is shown in Figure 4.2.

Since nickel is paramagnetic, the proton resonances of the nickel complex are shifted downfield, thus making the individual methyl and pyridine proton signals difficult to distinguish. Three separate peaks occur at δ 8.9, δ13.4 and δ44.4, which we have assigned to the host molecule protons, integrating for 28 protons.

A single, sharp signal appears at δ7.3 which is produced by the guest molecule, chloroform. This peak integrates for 1.8 protons, implying that there are 1.8 chloroform molecules per host. We realize that this result gives us a larger value than expected. This indicates that there is more chloroform in the solution, the excess of which may be assigned mainly to chloroform which had adhered to the surface of the crystals, and also to $CHCl_3$ impurity present in the deuterated solvent.

We note that no peaks appeared in the proton resonance region of p-Xylene.

Hence, in order to obtain meaningful results in such a study, we realize that the sample crystals have to be completely free of excess surface solvent.

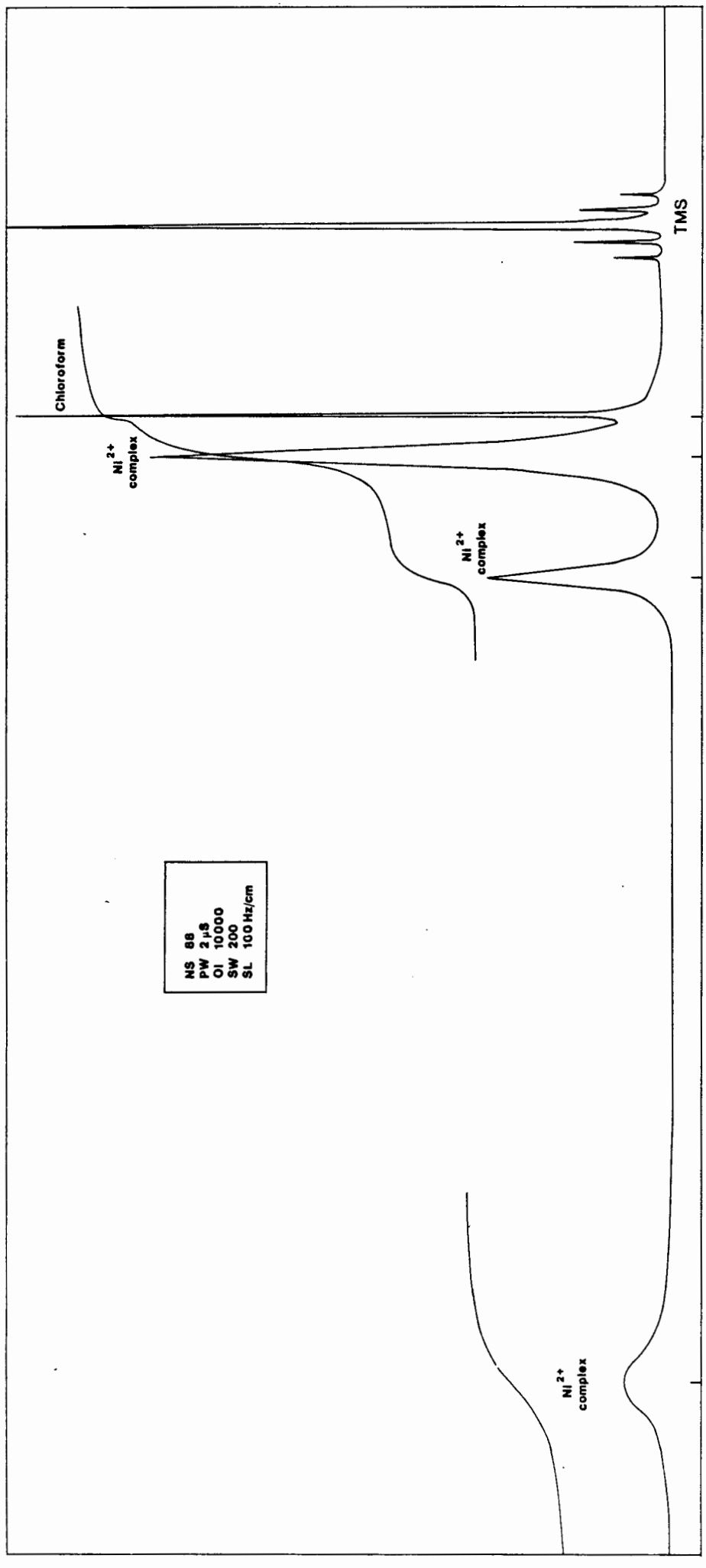


Figure 4.2 The ^1H N.M.R. Spectrum of $Ni(NCS)_2(3\text{-}MePy)_4.CHCl_3$

Analytical Determination of Nickel Content[61, 62, 63]

The nickel content of both the host and the clathrate complexes was determined quantitatively with high precision by complexiometric titration with ethylenediaminetetraacetic acid (EDTA) in ammoniacal solution using murexide as indicator.

The titration must be done with caution, since the sharpness of the colour change from orange to purple is highly pH dependent. It is sharpest in strongly alkaline solution just before the endpoint. Since the rate of formation of nickel-EDTA complex is not very high, the titration should be slow near the endpoint. However, this problem is by-passed by heating the solution to ~60°C, bearing in mind that the murexide sometimes decomposes rapidly in hot solutions.

General Procedure

All clathrate crystals were dabbed free of mother liquor before analysis.

To the accurately weighed-out nickel (host or clathrate) sample (not more than 15 mg of Ni per 100 ml) in a volumetric flask was added 10 ml HCl (0.5M) to break down the organic material. After allowing approximately 15 minutes for complete digestion, 10 ml NaOH (0.5M) was added to neutralize the solution, followed by 1 - 2 drops NH_4OH (5M) to raise the pH to 10-11. To this was added 10 ml NH_4Cl (1M) and a spatulaful of murexide indicator. The solution was heated to ~60°C, and EDTA solution (0.02498 M) added drop by drop. Once the colour of the solution changes from yellow to orange, and did not revert to yellow by the addition of a drop of conc. NH_3, the solution was made stongly ammoniacal by the addition of 10 ml conc. NH_3. The titration was continued to the colour change from deep-orange to purple.

From the titres one obtains the percentage nickel in the sample, from which is calculated the molecular weight of the sample by the relationship:

$$\text{MW (sample)} = \frac{\text{MW(nickel)}}{\text{percentage nickel}} \times 100$$

Now, MW (sample) - MW (host complex, 547.4 $g.mol^{-1}$)

= Molecular weight contribution by the guest species, namely chloroform; hence the number of moles of $CHCl_3$ present per mole of host complex.

Results

(i) Host complex, $Ni(NCS)_2(3\text{-}MePy)_4$

Weight of sample (mg)	19.8
Titre of EDTA (ml)	17.65
mmol of EDTA	0.03697
Weight of Ni^{2+} (mg)	2.17
% Ni^{2+}	10.96
Theoretical % Ni^{2+}	10.72

(ii) Clathrate, $Ni(NCS)_2(3\text{-}MePy)_4CHCl_3$

	Experiment		
	1	2	3
Weight of sample (mg)	21.9	21.4	19.5
Titre of EDTA (ml)	1.29	1.28	1.17
mmol of EDTA	0.0322	0.0320	0.0292
Weight of Ni^{2+} (mg)	1.89	1.88	1.72
% Ni^{2+}	8.64	8.77	8.80
MW of sample ($gmol^{-1}$)	679.51	669.36	667.23
Guest contribution ($gmol^{-1}$)	132.12	121.97	119.84
Host:Guest molar ratio	1:1.107	1:1.022	1:1.004

These results are consistent and prove with certainty that the ratio of host:guest is 1:1.

4.2 PRELIMINARY X-RAY ANALYSIS

The clathrate crystals were mounted with their mother liquor in Lindemann glass capillaries, due to their fast deterioration in air. Initial analysis involved ascertaining uniform extinction under plane polarized light. Oscillation and Weissenberg (zero- and upper-layer) photography indicated an orthorhombic space group with approximate cell parameters : a = 26Å, b = 24Å, c = 20Å and Z = 16.

Close investigation of the indexing of reflections showed the following conditions:

hkl : h + k, k + l, (l + h) = 2n
0kl : k + l = 4n (k, l = 2n)
h0l : h + l = 4n (h, l = 2n)
hk0 : h + k = 4n (h, k = 2n)
h00 : h = 4n
0k0 : k = 4n
00l : l = 4n

These are the conditions limiting possible reflections for the orthorhombic space group Fddd.

4.3 INTENSITY DATA COLLECTION

Mounted crystals were sent for diffractometer data collection to the C.S.I.R., Pretoria. Of the 2594 reflections collected within the range $3° < \theta < 23°$, 309 were systematically absent and 961 were omitted since they did not satisfy the criterion $I_{rel} < 2\sigma I_{rel}$, leaving 1324 reflections constituting the "observed" data. The relevant details of the data collection are tabulated in Table 4.2. No absorption correction was applied to the diffractometer data since the factor A* remained 1.5 over the entire range of θ scanned.

TABLE 4.2

CRYSTAL DATA AND REFINEMENT PARAMETERS FOR THE STRUCTURE ANALYSIS

Crystal Data

Molecular Formula	$NiC_{27}H_{29}N_6S_2Cl_3$
Molecular Weight	666.76 $g.mol^{-1}$
Space Group	Orthorhombic, Fddd
Z	16
a	26.28(1)Å
b	24.35(1)Å
c	21.47(1)Å
V	13736.59$Å^3$
D_m	1.31 $g.cm^{-3}$
D_c	1.29 $g.cm^{-3}$
μ (MoK_α)	13.04 cm^{-1}
μR	0.3
A*	1.5
F(000)	5504
Crystal dimensions	0.5 x 0.5 x 0.5 mm
Scan mode	ω- 2θ
Scan width	1.60°θ
Scan speed	0.053°θs^{-1}
Range scanned	3°<θ<23°
Stability of standard reflections	2.6%
Number of reflections collected	2594
Number of "observed" reflections	1324

Final Refinement

	Model A	Model B
Number of Variables	94	97
R	0.129	0.121
R_ω	0.147	0.133
Weighting scheme,ω	$(\sigma^2F + 0.008057\ F^2)^{-1}$	$(\sigma^2F + 0.008684\ F^2)^{-1}$

4.4 SOLUTION AND REFINEMENT OF THE STRUCTURE

The orthorhombic space group Fddd has two choices of origin, one at 222, at $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$ from $\bar{1}$, and the other at $\bar{1}$, at $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$ from 222. We chose the second origin. A diagram of the space group is shown in Figure 4.3.

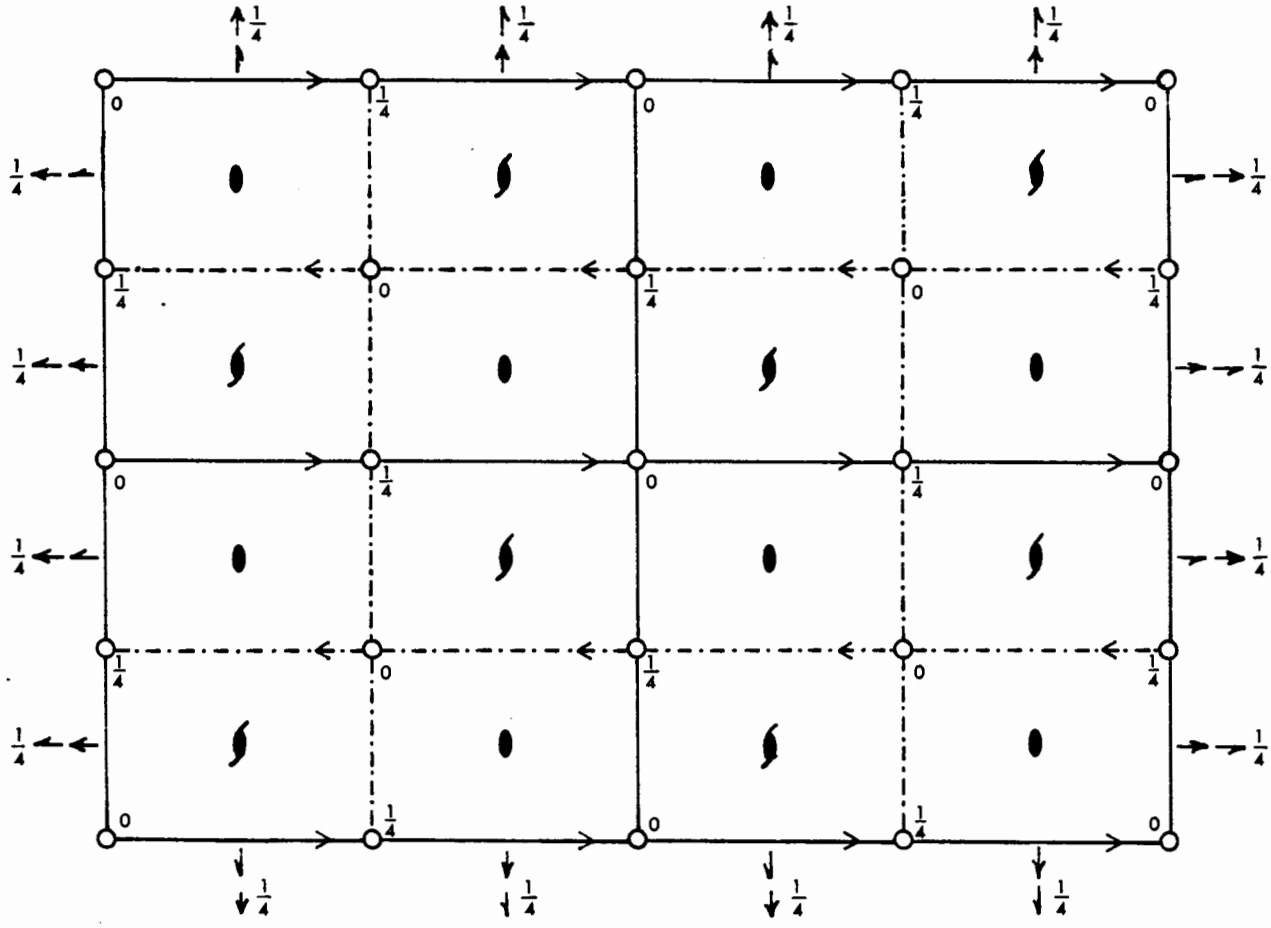


Figure 4.3 The space group Fddd

The coordinates of equivalent positions for Fddd are:

$(0, 0, 0 \;;\; 0, \tfrac{1}{2}, \tfrac{1}{2} \;;\; \tfrac{1}{2}, 0, \tfrac{1}{2} \;;\; \tfrac{1}{2}, \tfrac{1}{2}, 0) +$

$x, y, z \;;\; x, \tfrac{1}{4}-y, \tfrac{1}{4}-z \;;\; \tfrac{1}{4}-x, y, \tfrac{1}{4}-z \;;\; \tfrac{1}{4}-x, \tfrac{1}{4}-y, z \;;$

$-x, -y, -z \;;\; x, \tfrac{1}{4}+y, \tfrac{1}{4}+z \;;\; \tfrac{1}{4}+x, y, \tfrac{1}{4}+z \;;\; \tfrac{1}{4}+x, \tfrac{1}{4}+y, z,$

32 positions altogether.

Since the number of molecules per unit cell is 16, we suspect that the nickel atom lies on a special Wyckoff position, either c or d, which are on a centre of symmetry, or g, f or e which are on a two-fold axis, i.e.

c : $0, 0, 0 \;;\; 0, \tfrac{1}{4}, \tfrac{1}{4} \;;\; \tfrac{1}{4}, 0, \tfrac{1}{4} \;;\; \tfrac{1}{4}, \tfrac{1}{4}, 0$

d : $\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2} \;;\; \tfrac{1}{2}, \tfrac{3}{4}, \tfrac{3}{4} \;;\; \tfrac{3}{4}, \tfrac{1}{2}, \tfrac{3}{4} \;;\; \tfrac{3}{4}, \tfrac{3}{4}, \tfrac{1}{2}$

g : $\tfrac{1}{8}, \tfrac{1}{8}, z \;;\; \tfrac{1}{8}, \tfrac{1}{8}, \tfrac{1}{4}-z \;;\; \tfrac{7}{8}, \tfrac{7}{8}, -z \;;\; \tfrac{7}{8}, \tfrac{7}{8}, \tfrac{3}{4}+z$

f : $\tfrac{1}{8}, y, \tfrac{1}{8} \;;\; \tfrac{1}{8}, \tfrac{1}{4}-y, \tfrac{1}{8} \;;\; \tfrac{7}{8}, -y, \tfrac{7}{8} \;;\; \tfrac{7}{8}, \tfrac{3}{4}+y, \tfrac{7}{8}$

e : $x, \tfrac{1}{8}, \tfrac{1}{8} \;;\; \tfrac{1}{4}-x, \tfrac{1}{8}, \tfrac{1}{8} \;;\; -x, \tfrac{7}{8}, \tfrac{7}{8} \;;\; \tfrac{3}{4}+x, \tfrac{7}{8}, \tfrac{7}{8}$

$+ (0, 0, 0 \;;\; 0, \tfrac{1}{2}, \tfrac{1}{2} \;;\; \tfrac{1}{2}, 0, \tfrac{1}{2} \;;\; \tfrac{1}{2}, \tfrac{1}{2}, 0)$

A centrosymmetric direct methods program was run corresponding to the nickel atom lying on the diad at f, namely $\tfrac{1}{8}, y, \tfrac{1}{8}$ with y = 0.892.

A vector grid for this special position of the space group appears in Table 4.3.

TABLE 4.3

	$\frac{1}{8}$, y, $\frac{1}{8}$	$\frac{1}{8}$, $\frac{1}{4}$-y, $\frac{1}{8}$	$\frac{7}{8}$, y, $\frac{7}{8}$	$\frac{7}{8}$, $\frac{3}{4}$+y, $\frac{7}{8}$
$\frac{1}{8}$, y, $\frac{1}{8}$	0, 0, 0	0, $\frac{1}{4}$-2y, 0	$\frac{3}{4}$, -2y, $\frac{3}{4}$	$\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$
$\frac{1}{8}$, $\frac{1}{4}$-y, $\frac{1}{8}$	0, $\frac{3}{4}$+2y, 0	0, 0, 0	$\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$	$\frac{3}{4}$, $\frac{1}{2}$+2y, $\frac{3}{4}$
$\frac{7}{8}$, y, $\frac{7}{8}$	$\frac{1}{4}$, 2y, $\frac{1}{4}$	$\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$	0, 0, 0	0, $\frac{3}{4}$+2y, 0
$\frac{7}{8}$, $\frac{3}{4}$+y, $\frac{7}{8}$	$\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$	$\frac{1}{4}$, $\frac{1}{2}$-2y, $\frac{1}{4}$	0, $\frac{1}{4}$-2y, 0	0, 0, 0

+ (0, 0, 0 ; 0, $\frac{1}{2}$, $\frac{1}{2}$; $\frac{1}{2}$, 0, $\frac{1}{2}$; $\frac{1}{2}$, $\frac{1}{2}$, 0)

This gives the following vector types:

Vector Position	Multiplicity
0, 0, 0	4
$\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$	2
$\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$	2
0, $\frac{1}{4}$-2y, 0	2
0, $\frac{3}{4}$+2y, 0	2
$\frac{3}{4}$, -2y, $\frac{3}{4}$	1
$\frac{3}{4}$, $\frac{1}{2}$+2y, $\frac{3}{4}$	1
$\frac{1}{4}$, 2y, $\frac{1}{4}$	1
$\frac{1}{4}$, $\frac{1}{2}$-2y, $\frac{1}{4}$	1

The position of the nickel atom was confirmed by the subsequent Patterson map, from which the nickel atom was found to be located at the 0, $\frac{1}{4}$-2y, 0 vector position.

The first structure factor calculation was based on the nickel atom nearest the origin at $\frac{1}{8}$, $\frac{1}{4}$-y, $\frac{1}{8}$ at x = 0.125, y = 0.358, z = 0.125. The residual factor R was 0.46. Seven atoms were revealed in the electron density map, with interatomic distances agreeing well for isothiocyanate and pyridine groups. Insertion of these into a further structure factor calculation brought the R factor down to 0.317, and revealed a further eight atoms constituting the 3-methylpyridine (3-MePy) ring. From the following difference fourier map emerged the final two methyl groups of the 3-MePy ligands, thus completing the location of the atomic positions of the host molecule on an asymmetric unit, since it lies on a two-fold axis.

Three unidentifiable independent peaks were also revealed in the latter difference fourier. At this stage the R factor was only 0.202, thus we suspected that these other peaks belonged to the guest molecule.

Location of the guest

At this point, due to the uncertainty in the identification of the guest molecule, a difference fourier phased on the non-hydrogen host atoms of $Ni(NCS)_2(3\text{-}MePy)_4$ was computed, treating nickel and sulphur anisotropically, and electron density maps obtained in layers of 0.02 along the z axis. Each layer was traced onto a perspex sheet, and these placed on top of each other, presenting a three-dimensional picture of the cavity (see photograph in Figure 4.4). Regions of high electron density are coloured in red. R now decreased to 0.139.

A stick model of the host molecules in the unit cell was constructed to scale, such that the cavity due to their packing could be clearly visible and a reasonable model could be proposed for the location of the guest within.

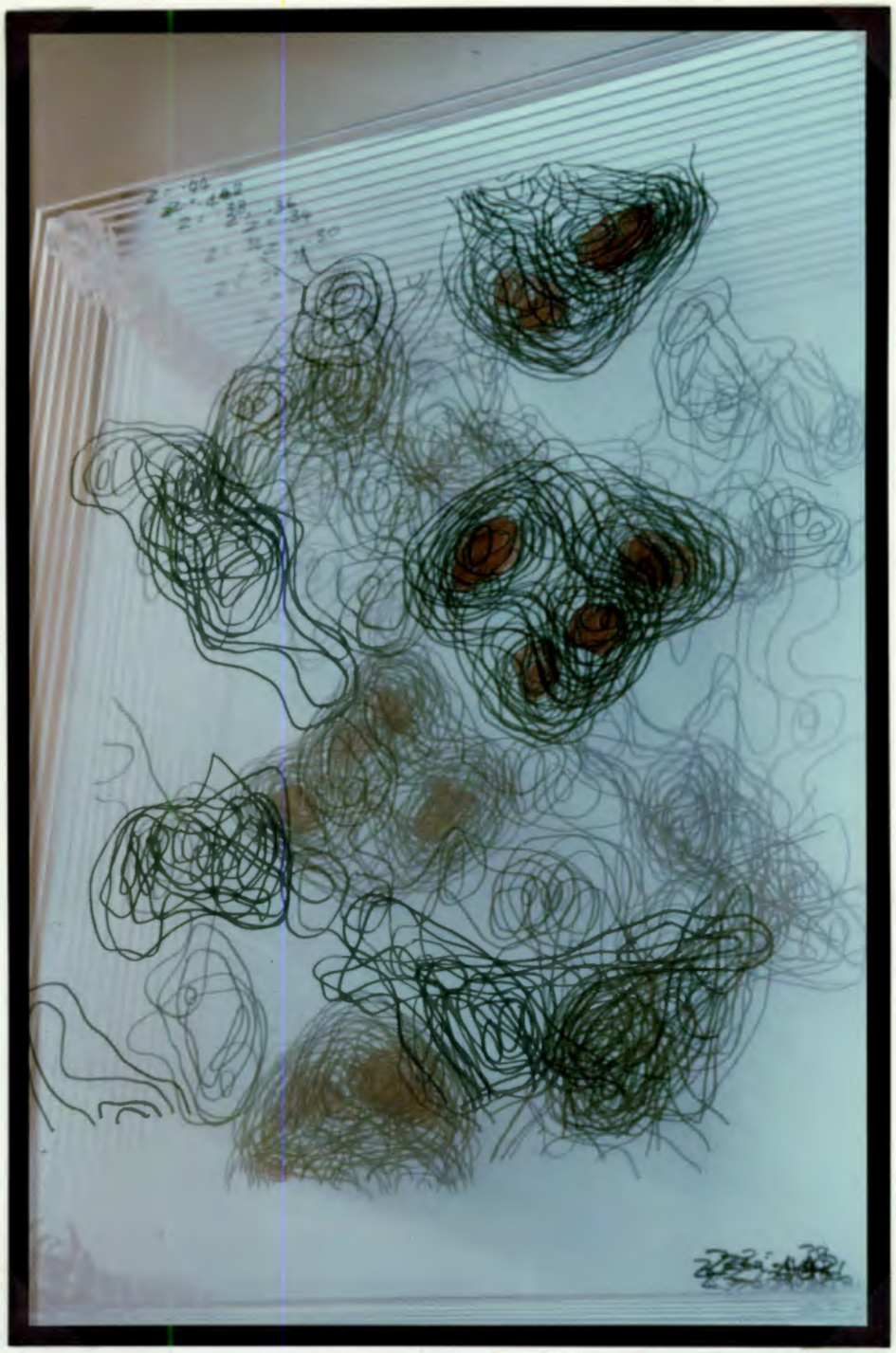


Figure 4.4 A Three-dimensional Electron Density Map, showing a quarter of the Unit Cell.

The electron-density search revealed four regions of very high electron density, about a two-fold axis of symmetry with the centre of the tetrahedron of much lower electron-density at approximately 0.5, 0.125, 0.125. Thus two of the four peaks are crystallographically symmetrical to each other. Fitting these four sets of coordinates, together forming a tetrahedron, into the cavity of the model, we saw that interatomic distances did not correlate at all with those of p-Xylene. We suspected that the four peaks belonged to the solvent, chloroform, the central peak being a carbon peak, since inter-peak distances related well with literature values for the Cl-Cl distance, namely Cl-Cl = 2.785(10)Å[16], calculated from an average C-Cl distance of 1.70Å. The question we now asked is : why four equally electron-rich peaks?

Model A

Refer to the diagram in Figure 4.5. Cl1, Cl2, Cl3 and Cl4 are the positions which emerged from the electron density map, all four being chlorine atoms. Two peaks were chosen i.e. Cl1 and Cl2, and their positions read off the electron density map layers. Peaks Cl3 and Cl4 are generated by symmetry.

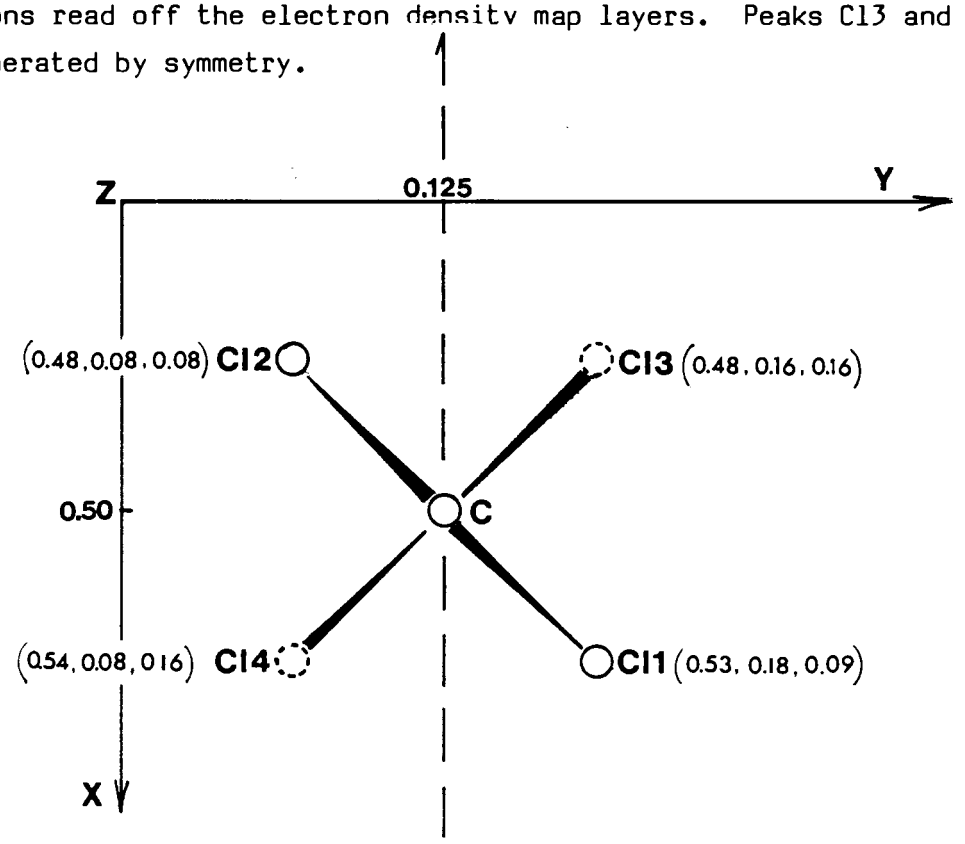


Figure 4.5

Assuming there is one chloroform molecule in this position, we proposed that each chlorine peak carried $\frac{3}{4}$ weight, such that through the symmetry conditions, $\frac{3}{4}$ x 4 peaks yields three chlorine atoms. Thus the site occupancy factor, s.o.f = 0.75.

The central carbon atom coordinates were chosen as 0.500, 0.125, 0.125, with y and z values fixed in the subsequent difference fourier. Even though the R factor refined to 0.131, the guest atoms displayed large thermal disorder, with thermal motion parameter values of approximately 0.26. It was also observed that the position of the carbon atom wandered along the X axis, also possessing high thermal motion parameters.

The R factor was further decreased in subsequent difference fourier runs, by inserting all aromatic and methyl protons of the host molecule, constrained to ride at 1.08 Å from their parent carbon atoms. Due to the thermal disorder of the chloroform molecule, it was necessary at this stage to apply bond length constraints. This involved inserting each of the four chlorine atoms separately, at refinable positions, and with the s.o.f. fixed at 0.375. The Cl-Cl distances were constrained to 2.785Å, with standard deviation of 0.010. The carbon atom coordinates, in the centre of the tetrahedron, were evaluated manually and fixed such that the bond lengths C-Cl were all 1.70(1)Å.

The final least-squares refinement involved constraining the guest molecule atomic distances and fixing the thermal parameters of the guest atoms at 0.20. The refinement converges to an R value of 0.129, and R_ω = 0.147, with the weighting scheme $\omega = (\sigma^2 F + 0.01265\ F^2)^{-1}$, which gives a satisfactory analysis of variance (Table 4.4).

Atomic coordinates and thermal parameters for the host and guest molecules of this model are listed in Table 4.5. Structure factors are listed in Appendix II.

Model B

Model A shows that the guest atoms have large thermal disorder. Temperature motion has the effect of spreading the electrons of an atom over a larger volume[64]. We observed, too, in the refinement calculations that some positions moved on refinement, and there were some peaks which were continually recurring, which were not fitted into Model A. For example, the Cl1 peak does at times appear at position 0.5206, 0.1983, 0.1025. This phenomenon occurs when the proposed model is slightly misplaced from the actual position, but its location still requires a small correction ϵ. (See Figure 4.6).

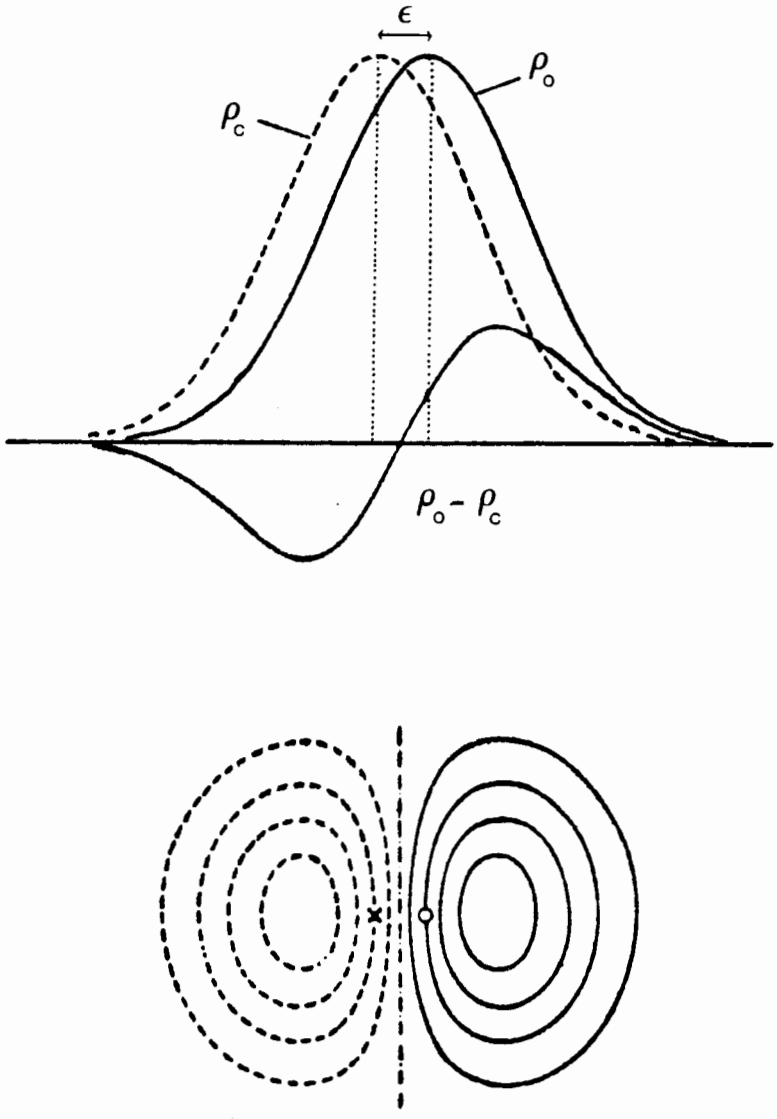


Figure 4.6

Thus the map $\rho_o - \rho_c$ contains a characteristic peak in the neighbourhood of the proposed location. Bearing this in mind, we can estimate the positioning of, for example, the chlorine atom Cl1.

Two peaks appeared during the refinement of Model A. These are positioned at (i) 0.5848, 0.1250, 0.1250

(ii) 0.4437, 0.1250, 0.1250,

both having site occupancy factors of 0.5, i.e. lying on the two-fold axis. Their low peak intensity could be attributed to their high temperature motion.

Model B

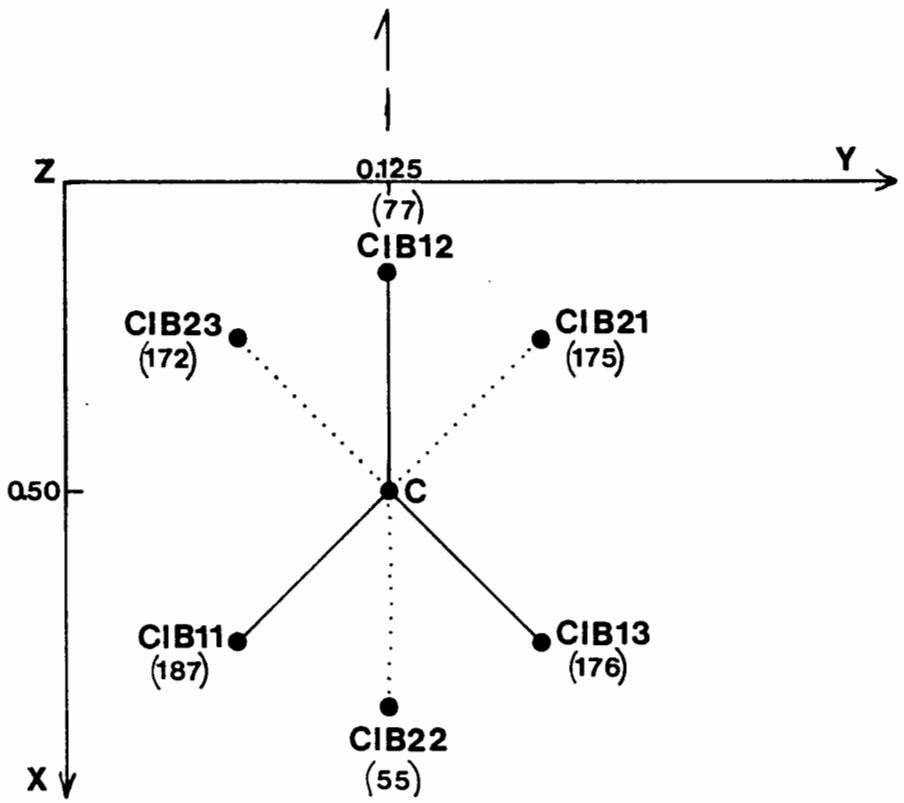


Figure 4.7

Now, by studying the relative peak heights from the electron density map of the six atomic positions labelled on the diagram (Figure 4.7), it was observed that the electron densities of the two proposed molecules are equal, thus making the two conformations equally probable. Thus, this second model assumes that the chloroform molecule spends half its time in position B1 (marked in solid lines), and the other half in position B2 (marked in dotted lines). We note that atoms B13 and B23 are symmetrically related to atoms B11 and B21 respectively. Thermal motion parameters were kept constant for all positions.

A number of refinement cycles were run with different weighting schemes to obtain the best analysis of variance and the most reasonable chemical model, where the inter-chlorine distances fell within 10% of the expected value of 2.785Å. The position of the central carbon atom was not defined.

The ultimate and most satisfactory least-squares refinement cycle yielded a residual factor $R = 0.120$ and $R_\omega = 0.133$, where the weighting scheme $\omega = (\sigma^2 F + 0.00807F^2)^{-1}$ was used. The site occupancy factors for the two positions of the guest molecule refined to 0.56 for B1 and 0.44 for B2.

The Analysis of Variance is listed in Table 4.6. Atomic coordinates and thermal motion parameters with their standard deviations, for the host and guest molecules are listed in Table 4.7. Structure factors may be found in Appendix III.

TABLE 4.4
ANALYSIS OF VARIANCE : MODEL A

a) By parity groups

Group	*ggg*	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*	All
N	614	0	0	0	0	0	0	710	1324
V	1871	0	0	0	0	0	0	1770	1818

b) As a function of $\sin\theta$

$\sin\theta$	0.00 - 0.16	0.20 - 0.23	0.26 - 0.29	0.31 - 0.33	0.35 - 0.37	0.39
N	138	132	127	150	167	119	113	132	132	114
V	3073	2163	2174	1555	1626	1438	1397	1393	1142	1167

c) As a function of $\sqrt{(F/F_{max})}$

$\sqrt{(F/F_{max})}$	0.00 - 0.18	0.19	0.20	0.21	0.23	0.25	0.27	0.31	0.38 - 1.00
N	244	116	106	88	158	124	93	130	138	127
V	2024	1691	1906	1611	1941	1639	2062	2016	1478	1476

d) As a function of |Miller index|

|h|	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	48	98	66	85	79	75	66	71	63	74	58	66	58	69	348
V	2106	1551	1800	1776	2056	2555	2034	1959	2326	2012	1781	1714	1824	1537	1419

|k|	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	60	53	78	55	92	69	84	76	72	82	57	79	33	75	359
V	1809	2250	1820	2298	1764	1877	1750	2433	2385	1659	2347	1791	1863	1424	1351

|l|	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	54	89	75	94	86	94	78	94	74	82	61	78	53	60	252
V	2216	2195	1676	2049	2067	1850	2092	1800	2122	1778	1818	1639	1604	1364	1392

N = No. of reflections in the group

V = 100 $[M\Sigma(\omega|F_o-F_c|^2)/N\Sigma\omega]$ where M = total no. of reflections

TABLE 4.5

FRACTIONAL ATOMIC COORDINATES ($\mathring{A} \times 10^4$) AND ISOTROPIC THERMAL PARAMETERS ($\mathring{A}^2 \times 10^3$) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES : MODEL A

Atom (Host)	x/a	y/b	z/c	U_{iso}
Ni(1)	1250(0)	3578(1)	1250(0)	a
N(1)	2033(5)	3577(6)	1320(6)	64(4)
C(1)	2441(6)	3690(6)	1403(7)	52(4)
S(1)	3039(2)	3837(2)	1547(3)	a
N(11)	1279(6)	4207(6)	545(6)	61(4)
C(12)	1648(7)	4213(7)	123(7)	60(4)
C(13)	1697(9)	4621(9)	-333(10)	88(6)
C(14)	1324(8)	5042(9)	-340(10)	91(6)
C(15)	920(9)	5006(10)	84(10)	99(7)
C(16)	920(7)	4583(8)	522(9)	72(5)
C(17)	2141(10)	4631(12)	-784(13)	126(9)
N(21)	1203(5)	2944(5)	1941(6)	55(3)
C(22)	874(6)	2557(7)	1907(8)	60(4)
C(23)	833(8)	2118(8)	2334(9)	70(5)
C(24)	1172(7)	2109(8)	2816(9)	78(6)
C(25)	1526(8)	2502(9)	2856(10)	90(6)
C(26)	1540(8)	2915(8)	2398(9)	74(5)
C(27)	402(9)	1711(11)	2282(12)	113(8)
H(12)	1914(7)	3919(7)	142(7)	b
H(14)	1344(8)	5353(9)	-644(10)	b
H(15)	638(9)	5281(10)	76(10)	b
H(16)	637(7)	4575(8)	833(9)	b
H(171)	2259(10)	5018(12)	-837(13)	c
H(172)	2398(10)	4420(12)	-538(13)	c
H(173)	2099(10)	4457(12)	-1203(13)	c
H(22)	613(6)	2562(7)	1549(8)	b
H(24)	1152(7)	1811(8)	3135(9)	b

Atom (Host)	x/a	y/b	z/c	U_{iso}
H(25)	1781(8)	2501(9)	3201(10)	b
H(26)	1816(8)	3198(8)	2414(9)	b
H(271)	222(9)	1693(11)	1874(12)	c
H(272)	614(9)	1374(11)	2338(12)	c
H(273)	147(9)	1736(11)	2627(12)	c

Atom (Guest)	x/a	y/b	z/c	U_{iso}
C(10)	2560(0)	3750(0)	3750(0)	d
CL(1)	2936(7)	3308(5)	3338(7)	d
CL(2)	2187(7)	4120(6)	3259(6)	d
CL(3)	2187(7)	3380(6)	4241(6)	d
CL(4)	2936(7)	4192(5)	4163(7)	d

a Anisotropic parameters of the form:

$$T = \exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}K^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*) \times 10^3]$$

with parameters

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni(1)	58(2)	42(2)	47(2)	0(0)	-1(2)	0(0)
S(1)	61(3)	99(4)	110(4)	27(3)	-4(3)	18(3)

b All H atoms have U_{iso} = 100 (0)

c All H atoms have U_{iso} = 150 (0)

d All Guest atoms have U_{iso} = 318 (9)

TABLE 4.6
ANALYSIS OF VARIANCE : MODEL B

a) By parity groups

Group	*ggg*	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*	All
N	614	0	0	0	0	0	0	710	1324
V	1674	0	0	0	0	0	0	1678	1676

b) As a function of sin θ

Sin θ	0.00 - 0.16	0.20 - 0.23	0.26 - 0.29	0.31 - 0.33	0.35 - 0.37	0.39
N	138	132	127	150	167	119	113	132	132	114
V	2580	2161	1861	1629	1558	1386	1265	1335	1081	1117

c) As a function of $\sqrt{(F/F_{max})}$

$\sqrt{(F/F_{max})}$	0.00 - 0.18	0.19	0.20	0.21	0.23	0.25	0.27	0.31	0.38 - 1.00
N	244	116	106	88	158	124	93	130	138	127
V	1915	1223	1882	1413	1780	1748	1773	1637	1373	1585

d) As a function of |Miller| index

|h|	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	48	98	66	85	79	75	66	71	63	74	58	66	58	69	348
V	1579	1474	1465	1323	1889	2738	1942	1466	2108	2046	1760	1761	1567	1378	1316

|k|	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	60	53	78	55	92	69	84	76	72	82	57	79	33	75	359
V	1666	2324	1534	1959	1490	1926	1828	1872	1761	1636	2052	1857	2161	1575	1259

|l|	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	54	89	75	94	86	94	78	94	74	82	61	78	53	60	252
V	1823	1950	1722	2062	1642	1774	1861	1681	1859	1607	1665	1583	1493	1397	1334

N = No. of reflections in the group
V = 100 $[M\Sigma(\omega|F_o-F_c|^2)/N\Sigma\omega]$ where M = total no. of reflections

TABLE 4.7

FRACTIONAL ATOMIC COORDINATES ($\mathring{A} \times 10^4$) AND ISOTROPIC THERMAL PARAMETERS ($\mathring{A}^2 \times 10^3$) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES : MODEL B

Atom (Host)	x/a	y/b	z/c	U_{iso}
Ni(1)	1250(0)	3579(1)	1250(0)	a
N(1)	2039(5)	3568(5)	1318(6)	63(3)
C(1)	2449(5)	3692(6)	1401(6)	50(4)
S(1)	3038(2)	3842(2)	1551(3)	a
N(11)	1275(5)	4205(5)	553(6)	60(3)
C(12)	1661(6)	4218(6)	122(7)	63(4)
C(13)	1698(8)	4622(7)	-343(8)	79(5)
C(14)	1333(7)	5023(8)	-338(9)	87(6)
C(15)	933(8)	5020(9)	91(9)	96(6)
C(16)	931(7)	4580(7)	520(8)	73(5)
C(17)	2132(9)	4651(10)	-768(12)	124(8)
N(21)	1204(5)	2947(5)	1943(6)	55(3)
C(22)	863(6)	2555(6)	1911(7)	63(4)
C(23)	830(7)	2117(7)	2335(8)	71(4)
C(24)	1175(7)	2120(8)	2817(8)	76(5)
C(25)	1540(8)	2503(8)	2842(9)	92(6)
C(26)	1552(7)	2920(7)	2397(8)	72(5)
C(27)	410(8)	1702(9)	2286(11)	106(7)
H(12)	1930(6)	3928(6)	140(7)	b
H(14)	1351(7)	5329(8)	-649(9)	b
H(15)	667(8)	5313(9)	97(9)	b
H(16)	638(7)	4554(7)	816(8)	b
H(171)	2467(9)	4482(10)	-663(12)	c
H(172)	1958(9)	4423(10)	-1091(12)	c
H(173)	2188(9)	5030(10)	-933(12)	c
H(22)	619(6)	2561(6)	1553(7)	b
H(24)	1154(7)	1836(8)	3152(8)	b

Atom (Host)	x/a	y/b	z/c	U_{iso}
H(25)	1807(8)	2488(8)	3174(9)	b
H(26)	1823(7)	3208(7)	2418(8)	b
H(271)	240(8)	1640(9)	1876(11)	c
H(272)	611(8)	1369(9)	2401(11)	c
H(273)	146(8)	1773(9)	2611(11)	c

Atom (Guest)	x/a	y/b	z/c	U_{iso}
CL1A	2836(9)	4299(10)	4082(11)	d
CL2A	1928(15)	3750(0)	3750(0)	d
CL1B	2298(12)	3368(12)	4164(13)	d
CL2B	3290(17)	3750(0)	3750(0)	d

a Anisotropic parameters of the form:

$$T = \exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}K^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*) \times 10^3]$$

with parameters

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni(1)	57(2)	42(1)	48(1)	0(0)	-1(1)	0(0)
S(1)	64(3)	102(4)	110(4)	29(3)	-3(3)	19(3)

b All H atoms have U_{iso} = 100 (0)

c All H atoms have U_{iso} = 150 (0)

d All Guest atoms have U_{iso} = 231 (6)

4.5 DESCRIPTION OF THE CLATHRATE STRUCTURE

(i) MOLECULAR STRUCTURE

Intramolecular bond lengths and angles, with estimated standard deviations, of the host and guest molecules, are given in Tables 4.8 and 4.9 respectively. Least-squares planes through various groups of atoms, and selected torsion angles are represented in Table 4.10. The parameters of the host molecule in Models A and B are very similar. Thus the following discussion is based on the parameters obtained for Model A.

The host molecule $Ni(NCS)_2(3\text{-}MePy)_4$ adopts a "windmill" conformation. The nickel atom is coordinated octahedrally to four 3-methylpyridine ligands and two isothiocyanate groups. A perspective view of the complex is shown in Figure 4.8. The molecule adopts two-fold axial symmetry. Pyridine ring N(11) generates N(31), while pyridine ring N(21) generates N(41) by virtue of this symmetry. We can describe the type of conformation of the host molecule by means of the four torsion angles between Ni-N (isothiocyanate) and the N-C bonds of each 3-methylpyridine ligand. In the crystalline structure of our host molecule these angles are (in order, clockwise, from N(11) to N(41)) : 145.0°, 143.1°, 142.4°, 147.7°. Thus we can denote this type of conformation (+ + + +) - the "windmill" conformation[19].

A schematic diagram of the environment around the nickel atom is given in Figure 4.9, indicating bond lengths and angles found. The atoms N(11), N(21), N(31) and N(41) are coplanar. Angles subtended by nickel in this plane deviate from 90° by small amounts, ranging from 88.0(4)° for N(21) - Ni(1) - N(41) to 91.(4)° for N(21) - Ni(1) - N(31).

It is a common feature of these structures that the average Ni-N bond length for the pyridine rings (2.150(10)Å) is considerably longer than the Ni-N distance of the isothiocyanate group (2.062(11)Å), the difference being more than eight times greater than the standard deviation. As described in Chapter 3, this difference has been attributed to the non-bonded interactions within the molecule.

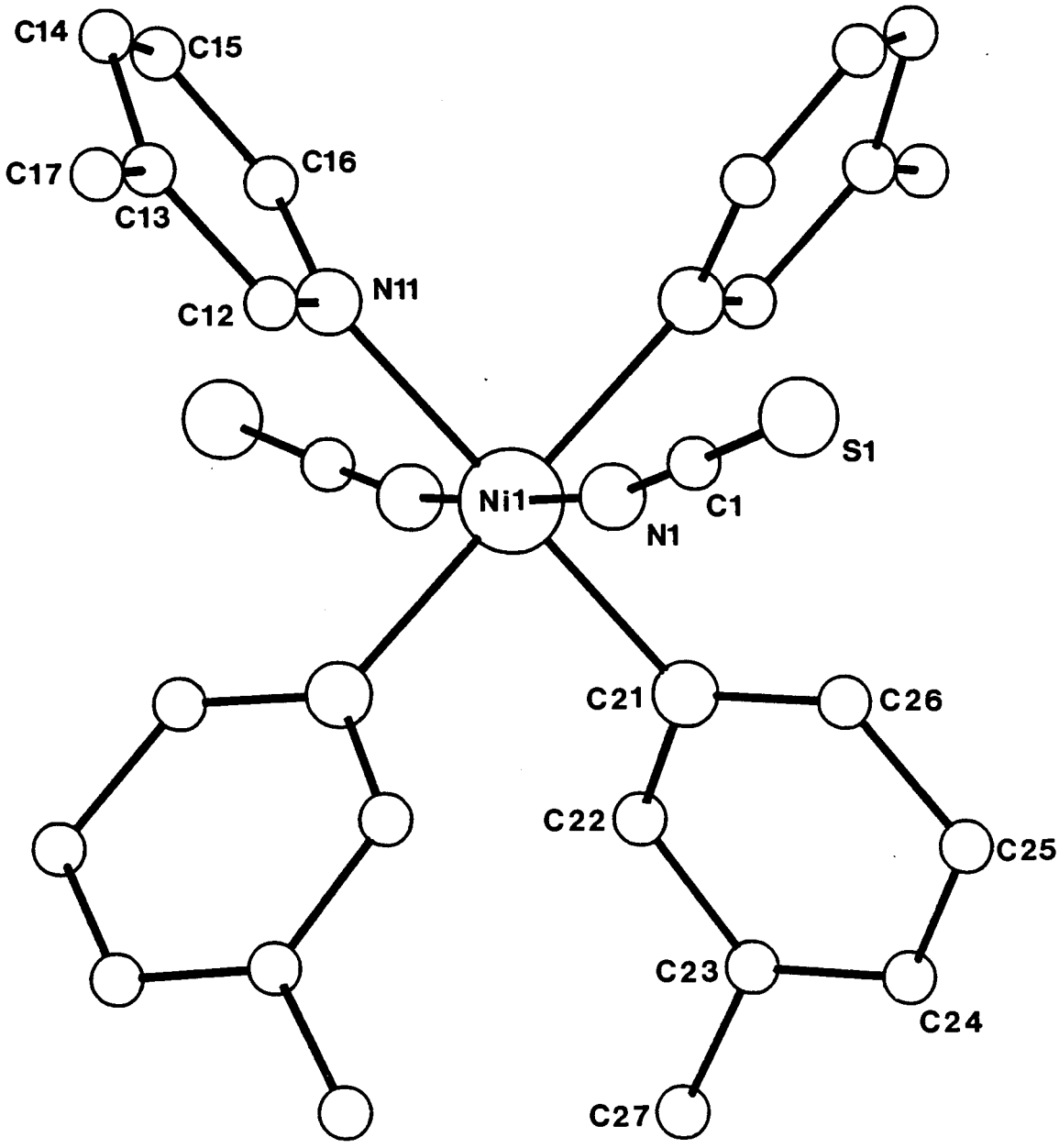


Figure 4.8 The Host Complex $Ni(NCS)_2(3\text{-methylpyridine})_4$

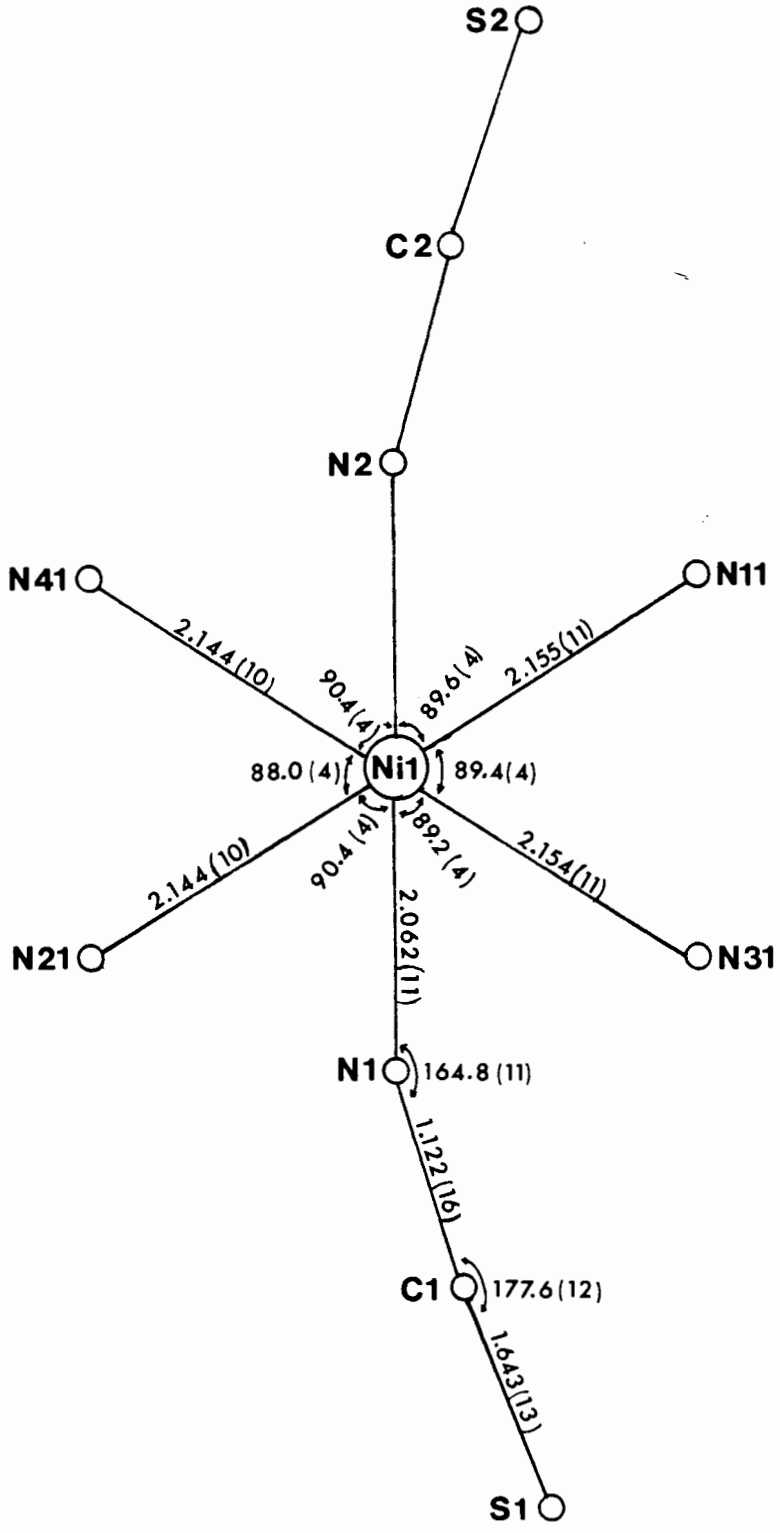
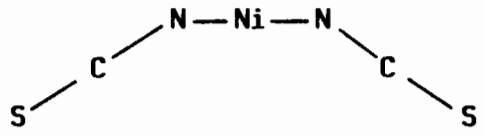
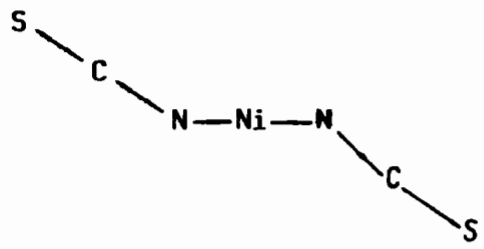


Figure 4.9 The Environment of the Nickel Atom indicating Bond Lengths (Å) and Angles (°)

The two-fold symmetry of the space group causes the NCS group to be arranged such:



instead of the following:



The angle N(1) - Ni(1) - N(2) is 179.8(4)°, while angles subtended by nickel from the isothiocyanate groups to the pyridine ligands are an average of 90(1)°.

As is observed from the diagram, the isothiocyanate ligands themselves are not linear. The angle Ni(1) - N(1) - C(1) is 164.8(11)°.

Least-squares planes were evaluated for the pyridine rings N(11) and N(21), and their symmetry-related rings N(31) and N(41). The rings are planar to within 0.03Å, and twisted with respect to the plane defined by N(11) - N(21) - N(31) - N(41) (Plane 5).

The rotation of the Ni-N (pyridine) bond may be described in terms of the dihedral angles with respect to Plane 5. Ring N(11) is twisted by 55.8(10)°; ring N(21) by 52.9(10)°; ring N(31) by 52.8(10)° and ring N(41) by 56.7(10)°, all twists being of the same magnitude.

The pyridine ligands in trans-positions are also twisted with respect to each other. These torsion angles, however, vary between Models A and B. For Model A, the trans-dihedral angle between N(11) and N(21) is 9.7(9)°, and between N(31) and N(41) 8.3(9)°. However, Model B exhibits trans-dihedral angles of 23.1(10)° between N(11) and N(21) and 24.0(10)° between N(31) and N(41).

This variation in twist demonstrates the ease with which the host complex is able to "adjust" its molecular shape, to make possible the clathration of guest molecules of different size. In the present structure, the proposed positioning and shape of the guest are different in Models A and B.

TABLE 4.8

BOND LENGTHS (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Host Molecule

	Model A	Model B
Ni(1) - N(1)	2.062(11)	2.079(14)
Ni(1) - N(11)	2.155(11)	2.136(13)
Ni(1) - N(21)	2.144(10)	2.143(13)
N(1) - C(1)	1.122(16)	1.133(19)
C(1) - S(1)	1.643(13)	1.623(16)
N(11) - C(12)	1.330(15)	1.374(20)
N(11) - C(16)	1.316(17)	1.288(21)
C(12) - C(13)	1.399(20)	1.404(24)
C(13) - C(14)	1.420(23)	1.369(27)
C(13) - C(17)	1.515(25)	1.464(30)
C(14) - C(15)	1.401(22)	1.396(27)
C(15) - C(16)	1.393(22)	1.414(27)
N(21) - C(22)	1.280(15)	1.311(19)
N(21) - C(26)	1.324(17)	1.338(21)
C(22) - C(23)	1.412(19)	1.404(23)
C(23) - C(24)	1.365(20)	1.377(25)
C(23) - C(27)	1.508(22)	1.500(27)
C(24) - C(25)	1.338(21)	1.339(26)
C(25) - C(26)	1.406(21)	1.394(26)
All C - H bond lengths	1.080(18)	1.080(18)

Guest Molecule

	Model A
C(10) - CL(1)	1.708(9)[a]
C(10) - CL(2)	1.699(9)[a]
C(10) - CL(3)	1.699(9)[a]
C(10) - CL(4)	1.708(9)[a]

a bond lengths fixed

	Model B
CL(1A) - CL(2A)	2.825(9)[b]
CL(2A) - CL(3A)	2.825(9)[b]
CL(1A) - CL(3A)	3.031(9)[b]
CL(1B) - CL(2B)	2.920(9)[b]
CL(2B) - CL(3B)	2.920(9)[b]
CL(1B) - CL(3B)	2.576(9)[b]

b These values were calculated on an Apple mini-computer by a program calculating bond lengths and angles.

TABLE 4.9

BOND ANGLES (DEGREES) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Host Molecule

	Model A	Model B
N(11) - Ni(1) - N(1)	91.0(4)	91.5(5)
N(21) - Ni(1) - N(1)	90.4(4)	90.0(5)
N(21) - Ni(1) - N(11)	178.5(4)	178.5(5)
C(1) - N(1) - Ni(1)	164.8(11)	163.0(13)
S(1) - C(1) - N(1)	177.6(2)	176.7(15)
C(12) - N(11) - Ni(1)	120.9(9)	120.8(11)
C(16) - N(11) - Ni(1)	119.8(10)	121.5(12)
C(16) - N(11) - C(12)	119.3(12)	117.7(15)
C(13) - C(12) - N(11)	123.6(13)	123.1(16)
C(14) - C(13) - C(12)	117.1(16)	116.5(19)
C(17) - C(13) - C(12)	121.9(16)	122.1(20)
C(17) - C(13) - C(14)	120.9(17)	121.1(20)
C(15) - C(14) - C(13)	118.1(17)	121.8(21)
C(16) - C(15) - C(14)	119.0(17)	115.9(21)
C(15) - C(16) - N(11)	122.7(14)	124.8(18)
C(22) - N(21) - Ni(1)	122.0(9)	121.7(11)
C(26) - N(21) - Ni(1)	120.8(9)	120.2(11)
C(26) - N(21) - C(22)	117.0(12)	117.9(15)
C(23) - C(22) - N(21)	124.9(13)	124.2(16)
C(24) - C(23) - C(22)	117.0(14)	116.3(18)
C(27) - C(23) - C(22)	120.4(14)	120.8(17)
C(27) - C(23) - C(24)	122.3(15)	122.7(18)
C(25) - C(24) - C(23)	119.4(16)	120.4(20)
C(26) - C(25) - C(24)	119.0(16)	119.7(20)
C(25) - C(26) - N(21)	122.6(15)	121.4(18)
CL(4) - C(10) - CL(1)	109.3(9)	not defined
CL(2) - C(10) - CL(1)	110.3(3)	not defined
CL(2) - C(10) - CL(4)	108.8(3)	not defined
CL(3) - C(10) - CL(1)	108.8(3)	not defined
CL(3) - C(10) - CL(4)	110.3(3)	not defined
CL(3) - C(10) - CL(2)	109.5(9)	not defined

TABLE 4.10

LEAST-SQUARES PLANES AND TORSION ANGLES : MODELS A AND B

1(a) Equations of Least-Squares Planes expressed in Orthogonalised Space as pX + qY + rZ = S

Plane 1: The pyridine ring atoms [N(11), C(12), C(13), C(14), C(15), C(16)]

A	14.1008	X	-13.6290	Y	+13.5567	Z	= 15.1291
B	14.3475	X	-13.5948	Y	+13.4099	Z	= 15.1223

Plane 2: The pyridine ring atoms [N(21), C(22), C(23), C(24), C(25), C(26)]

A	16.2999	X	+13.3704	Y	-12.0250	Z	= -2.5504
B	15.9345	X	+13.4545	Y	-12.2763	Z	= -2.9079

Plane 3: The pyridine ring atoms [N(31), C(32), C(33), C(34), C(35), C(36)]

A	14.1614	X	+13.6131	Y	+13.5269	Z	= 19.1622
B	14.3736	X	+13.5714	Y	+13.4097	Z	= 19.1127

Plane 4: The pyridine ring atoms [N(41), C(42), C(43), C(44), C(45), C(46)]

A	-16.2808	X	+13.3536	Y	+12.0568	Z	= 6.2982
B	-15.9387	X	+13.4470	Y	+12.2790	Z	= 6.6226

Plane 5: The molecular plane defined by atoms [N(11), N(21), N(31), N(41)]

A	26.2231	X	- 0.0006	Y	+ 1.4241	Z	= 11.0797
B	26.2291	X	- 0.0104	Y	+ 1.3485	Z	= 11.0150

1(b) Deviations of Selected Atoms from the Planes ($\mathring{A} \times 10^3$)
($\sigma \times 10^3 < 30$)

Atom	Plane 1		Atom	Plane 3	
	Model A	Model B		Model A	Model B
Ni(1)	83	60	Ni(1)	-80	-61
N(11)*	25	12	N(11)	-1849	-1809
C(12)*	-21	6	N(21)	1653	1660
C(13)*	-6	-16	N(31)*	-24	-12
C(14)*	28	-10	C(32)*	17	-6
C(15)*	-25	7	C(33)*	9	16
C(16)*	-1	-19	C(34)*	-27	-10
C(17)	24	79	C(35)*	21	-6
N(21)	90	64	C(36)*	4	18
N(31)	1855	1810	C(37)	-24	-77
N(41)	-1652	-1661	N(41)	-85	-65

Atom	Plane 2		Atom	Plane 4	
	Model A	Model B		Model A	Model B
Ni(1)	42	53	Ni(1)	45	55
N(11)	96	107	N(11)	-1692	-1682
N(21)*	-19	-20	N(21)	1802	1829
C(22)*	4	3	N(31)	102	109
C(23)*	8	21	N(41)*	-18	-21
C(24)*	-7	-27	C(42)*	4	4
C(25)*	-7	9	C(43)*	9	20
C(26)*	20	15	C(44)*	-8	-26
C(27)	-88	-28	C(45)*	-5	10
N(31)	-1694	-1684	C(46)*	18	14
N(41)	1798	1829	C(47)	-87	-30

* Atoms used to calculate the least-squares plane.

1(c) Angles between Normals to Planes (°)

	Model A	Model B
Plane 1 and 2	109.2	109.6
" 1 " 3	68.0	67.8
" 1 " 4	106.5	106.4
" 1 " 5	54.7	54.2
" 2 " 3	73.2	73.6
" 2 " 4	113.4	112.9
" 2 " 5	54.4	55.3
" 3 " 4	70.9	70.5
" 3 " 5	54.6	54.2
" 4 " 5	125.5	124.7

2. Selected Torsion Angles (°)

	Model A	Model B
C(16) - N(11) - Ni(1) - N(31)	55.8	55.9
C(32) - N(31) - Ni(1) - N(21)	52.8	54.0
C(22) - N(21) - Ni(1) - N(41)	52.9	53.7
C(46) - N(41) - Ni(1) - N(11)	56.7	57.5
N(11) - Ni(1) - N(21) - C(22)	-9.7	-23.1
N(31) - Ni(1) - N(41) - C(42)	-8.3	-24.0
N(1) - Ni(1) - C(11) - C(16)	145.0	145.3
N(1) - Ni(1) - N(31) - C(32)	143.1	143.9
N(1) - Ni(1) - N(21) - C(22)	142.4	142.7
N(1) - Ni(1) - N(41) - C(46)	147.7	149.0

(ii) MOLECULAR PACKING

The host molecules form a lattice framework very typical of the zeolite-type packing exhibited by many β-type clathrates of $Ni(NCS)_2(4\text{-}MePy)_4$. The packing demonstrates both channel- and cage-type behaviour.

There are sixteen host molecules in the unit cell which from the clathrating framework. The packing is shown in Figures 4.10 and 4.11. The nickel atoms lie on the diads running parallel to the Y axis, but any two host molecules packed directly above each other along X are shifted with respect to each other by small amounts about the diad running parallel to Z. It is this that brings about the formation of cavities.

Viewing the cell down X we see that voids are formed which are diamond-shaped in cross-section. This view is in fact virtually perpendicular to the N(11)- N(21)- N(31)- N(41) plane. Isothiocyanate groups are parallel to the X axis. Thus channels are formed which run parallel to X.

However, by virtue of the cell symmetry and the packing of the host molecules, these channels are wider in one half of the cell, producing a cage in which two guest molecules are trapped. To explain this effect diagrammatically, refer to Figure 4.12. This is a view of the unit cell down Z from z=0 to the z=0.5. Host molecules 1 and 2 are positioned further apart than host molecules 3 and 4, forming a larger cage in the former case. The cavity is widest when the nickel atoms of the host molecules at the same z level are furthest apart along y. Furthermore, there is large steric hindrance caused by the bulky methyl groups in the latter case. Thus this void can in no way accommodate any guest molecules.

The two chloroform molecules are located in this cage on a two-fold axis, and are both disordered.

Overall, the cage/channel voids can be pictured as taking an hour-glass shape. There are eight such channels where the widest part of one channel fits into the narrowest part of the other. The positions of the guest molecules are labelled in Figure 4.13.

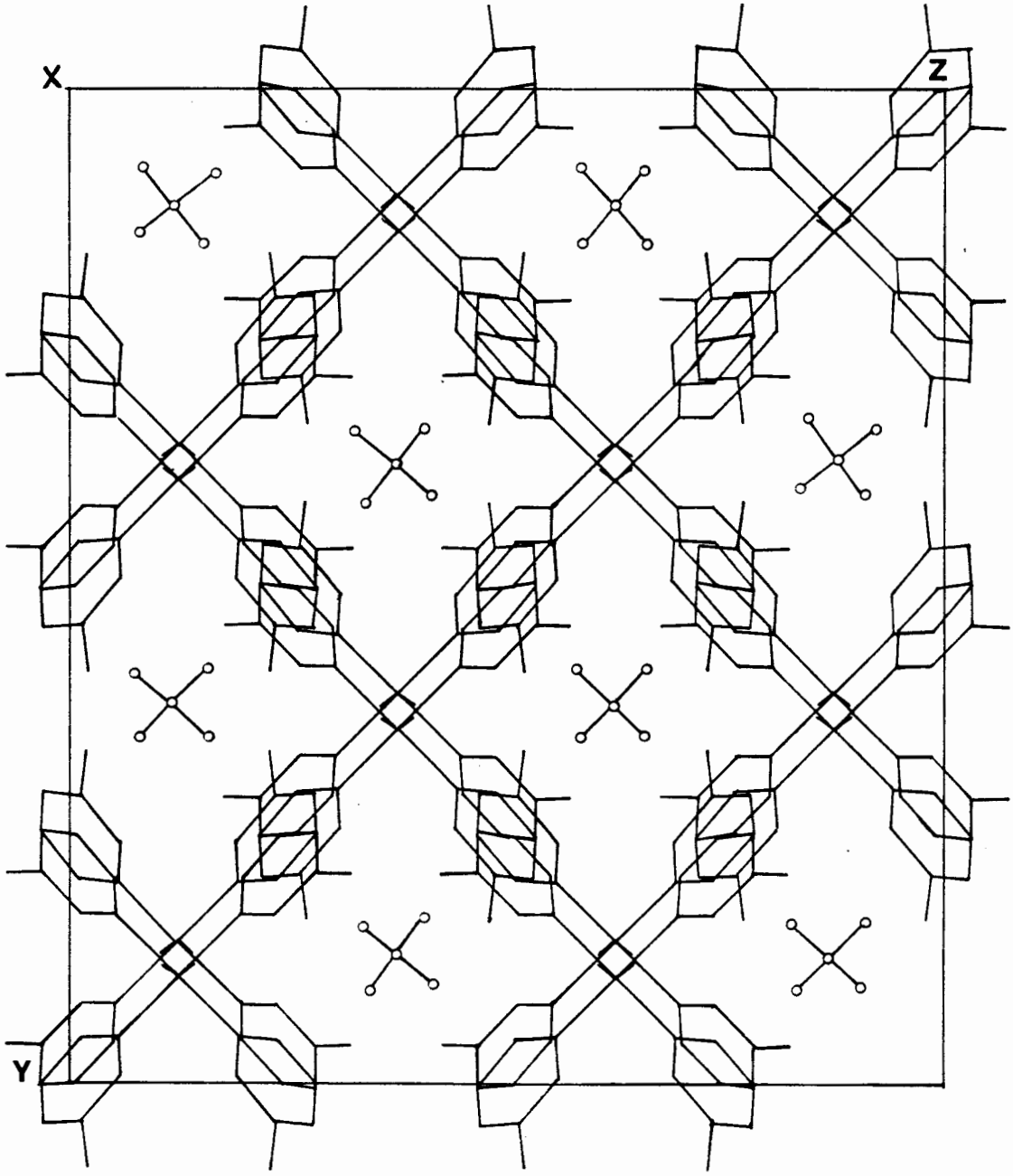


Figure 4.10 Molecular Packing of $Ni(NCS)_2(3\text{-}MePy)_4.CHCl_3$, viewed down the X axis

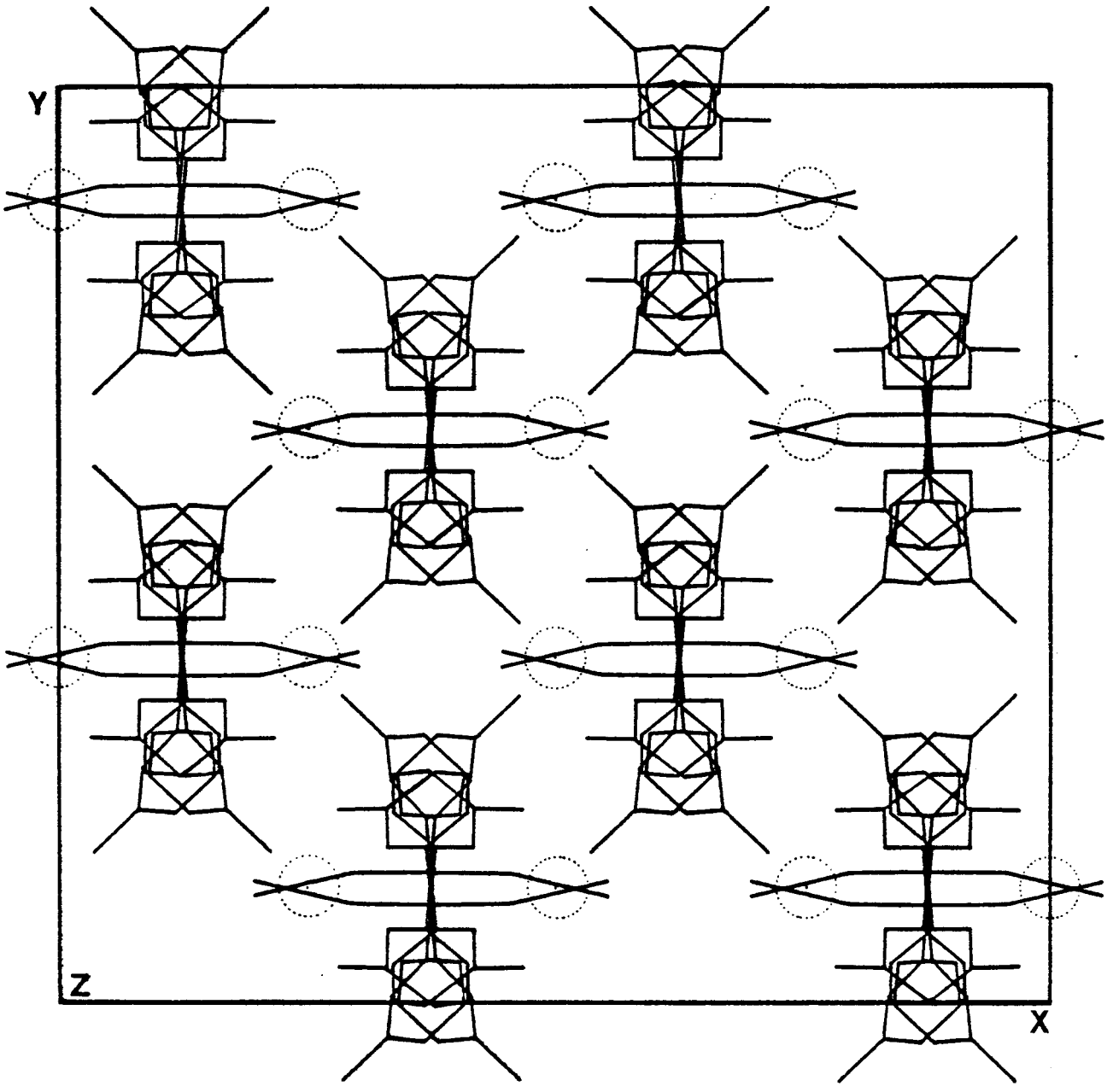


Figure 4.11 Molecular packing, viewed down the Z axis

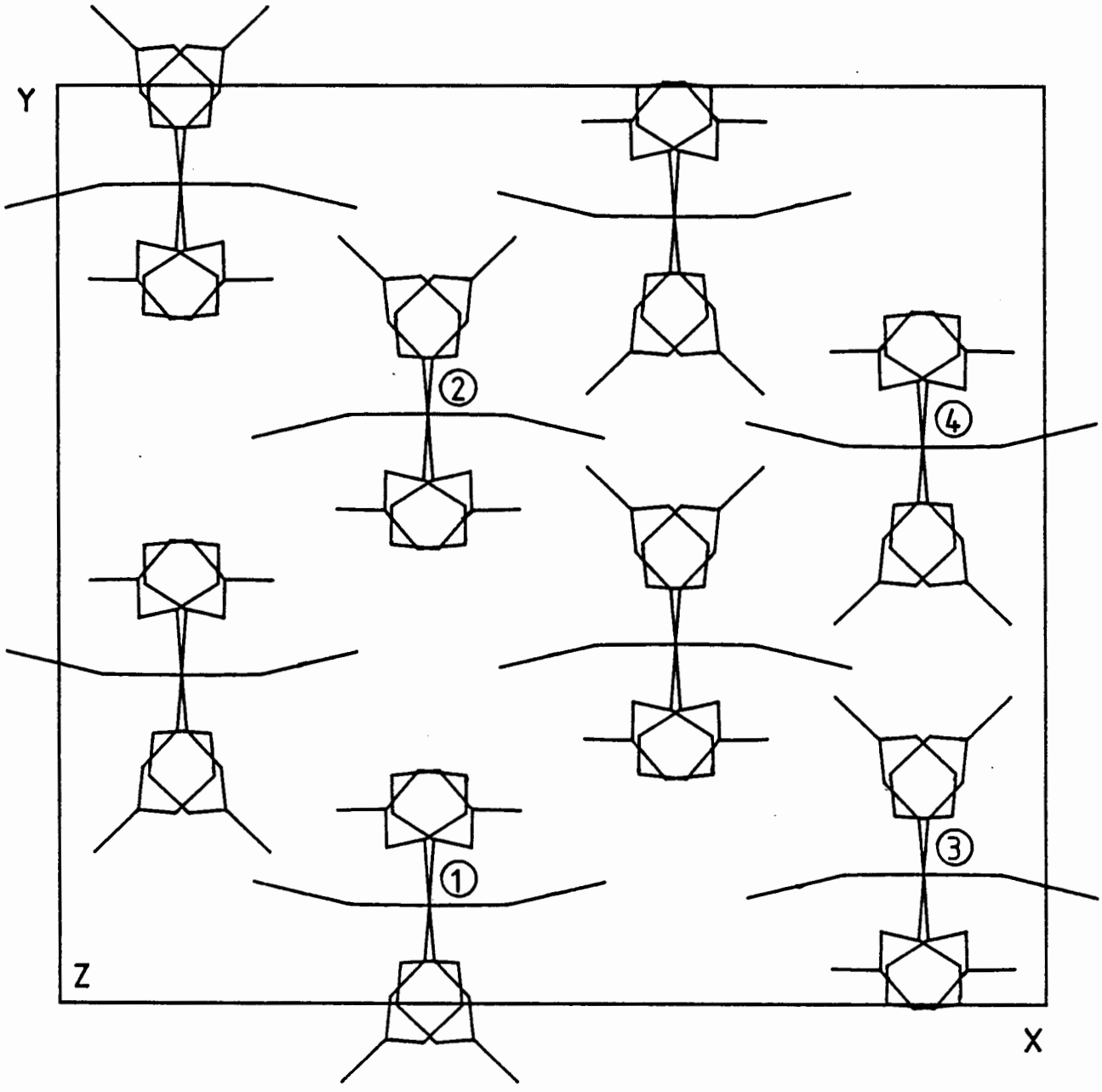


Figure 4.12 Molecular packing, viewed down the Z axis

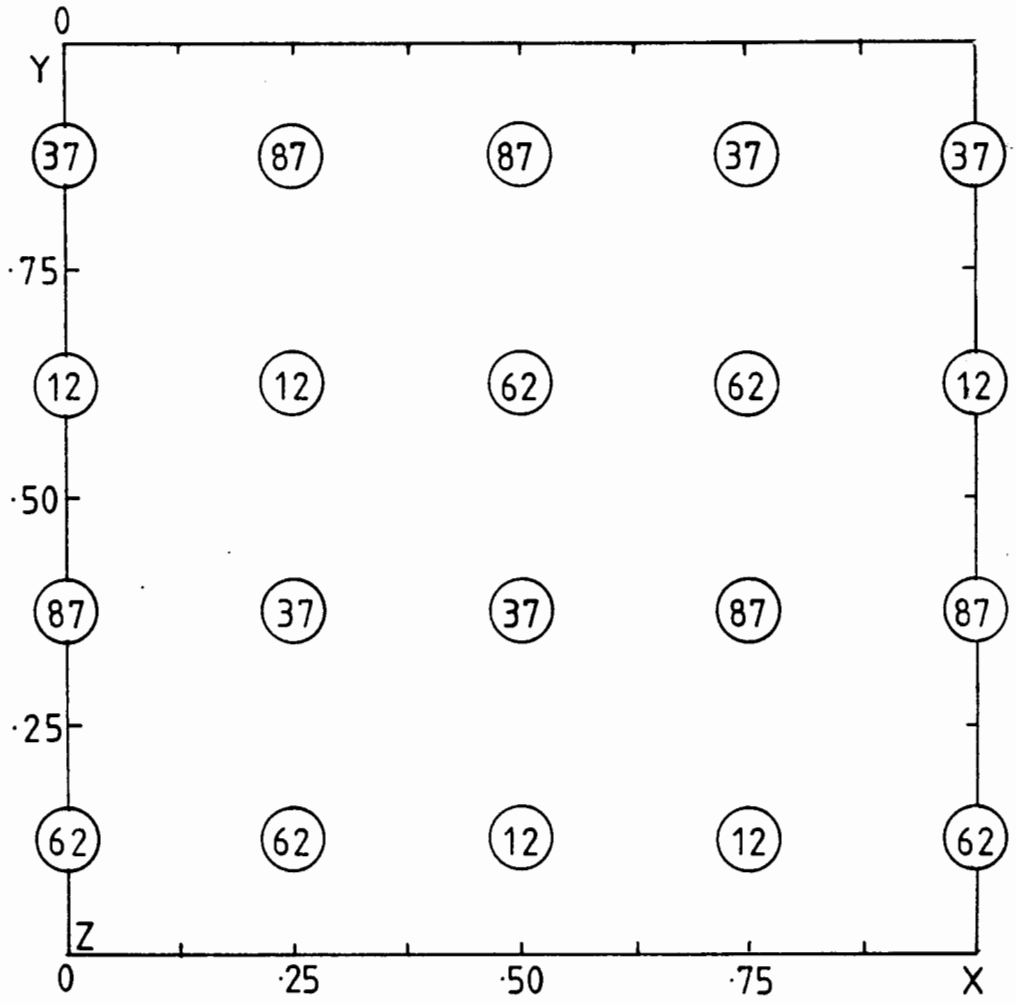


Figure 4.13 The Guest Molecules in one Unit Cell indicating their Heights along Z

CHAPTER 5

CHAPTER 5

AN INVESTIGATION OF THE ZEOLITIC NATURE OF THE CHLOROFORM-CONTAINING CLATHRATE

5.1 INTRODUCTION

In the absence of guest molecules in solution the host complex crystalizes in its "non-clathrating" crystalline form denoted as α [19, 65, 66]. In the presence of guests which form inclusion compounds with the host molecules, the clathrating structure modification of the Werner complex is defined as β when cage and channel-type clathrates are formed, and γ when the packing is of the layer-type.

Thus the reaction with which we are dealing is:

$$\alpha\text{- Ni(NCS)}_2\text{(substituted pyridine)}_4 + nG \rightleftharpoons \beta\text{- Ni(NCS)}_2\text{(substituted pyridine)}_4.nG$$

where G denotes the guest species.

Now, in the β-phase clathrates, escape of the guest molecules is possible without destroying the crystalline framework of the host; thus the β-phase may be regarded as an "organic zeolite" behaving like crystals that are permanently porous in the absence of guest molecules, and their sorption isotherms are reversible [23, 67]. The strains caused by lattice contraction as the guest is desorbed may cause "cracking" of β- $Ni(NCS)_2$(substituted pyridine)$_4$.G crystals the crystals then become non-transparent, and this allows us to estimate the stability of the clathrate visually [28, 68].

The aim of the experiment performed in this study is to investigate whether the β-phase structure of the clathrate β-$Ni(NCS)_2(3\text{-MePy})_4.CHCl_3$ is retained after complete guest desorption:

$$\beta_1\text{-Ni(NCS)}_2\text{(3-MePy)}_4\text{.CHCl}_3 \longrightarrow \beta_0\text{- Ni(NCS)}_2\text{(3-MePy)4 + CHCl}_3$$

where β_0 denotes the "empty" β- structure, which should in fact be independent of the guest[19].

5.2 EXPERIMENTATION AND RESULTS

Apparatus and General Procedure

The way in which we determine whether the host framework has collapsed after guest desorption, or has attained a different crystalline form, is by taking X-ray powder photographs of the clathrate crystals before guest desorption, during the desorption process and finally after all the guest species has escaped[69]. The relationship of the diffraction angle to the measured arc length S, read off the resulting powder lines, is given by [70].

$$\frac{4\theta}{360} = \frac{S}{2\pi r} \quad \text{where } r = 28.65 \text{ mm}$$

Each Bragg angle θ for a particular line is readily transformed into the interplanar spacing d_{hkl} for the plane responsible for the reflection to that line, by the relationship

$$\lambda = 2d\sin\theta$$

where λ = wavelength

On comparing the d-spacings of the powder lines and their relative intensities at these different stages, we may observe and identify any structural changes which might have occurred. The percentage carbon, hydrogen and nitrogen present at each step of the experiment is determined by microanalysis. This method also provides a stoicheiometric determination of the clathrate.

The apparatus used was a sorption balance attached to a vacuum line. Since its introduction by McBain and Bakr [71] in 1926, this silica spring balance has been an important and successful means of studying the sorption and desorption of vapours and gases by solids, not only at ordinary temperatures and pressures but also at high pressures and low temperatures and in corrosive atmospheres[72].

The apparatus, represented diagramatically in Figure 5.1, consists essentially of a spring balance, the spring being made of a fine silica fibre. To the end of the spring is attached a small, light glass bucket, used as the container for the sample. The length of the extended spring when supporting the bucket is then read in a travelling telescope. The spring plus bucket are enclosed in a wide, straight glass tube, about 30 cm long and 7 cm in diameter, which is attached to a high vacuum system. The whole system may be heated by surrounding the glass tube with a heating coil.

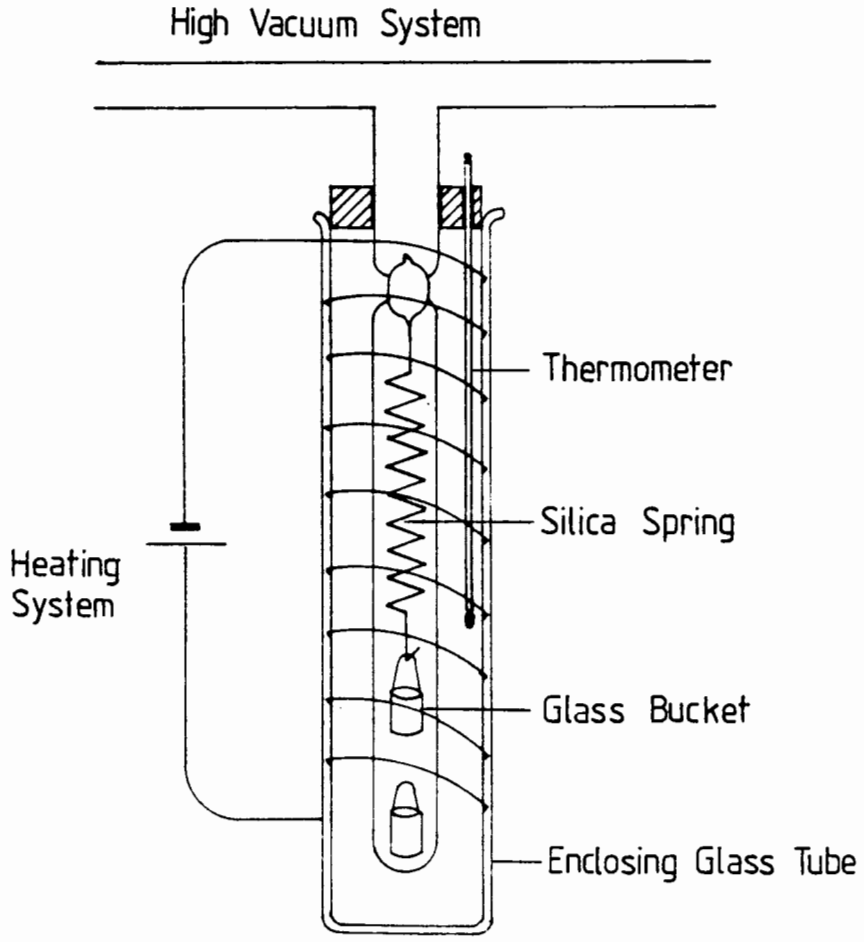


Figure 5.1 The McBain Spring Balance

The principal involved here is simply Hooke's Law, $f = -kx$

where $f = mg$ = weight of a known mass

x = displacement of spring

k = spring constant

Calibration of the Spring (under vacuum, pressure = 77.75 mmHg)

TABLE 5.1

Accumulated Weight (mg)	Height (cm)	x
0	44.544	
99.8	43.142	1.402
200.0	41.752	1.390
299.8	40.343	1.409
400.1	38.948	1.395
499.9	37.569	1.379
599.9	36.181	1.388

Height was plotted versus accumulated weight. The calibration curve presented in Figure 5.2 is linear, implying a reliably sensitive spring. The slope gives a value of 0.01399 $cm.mg^{-1}$, which does not change with temperature.

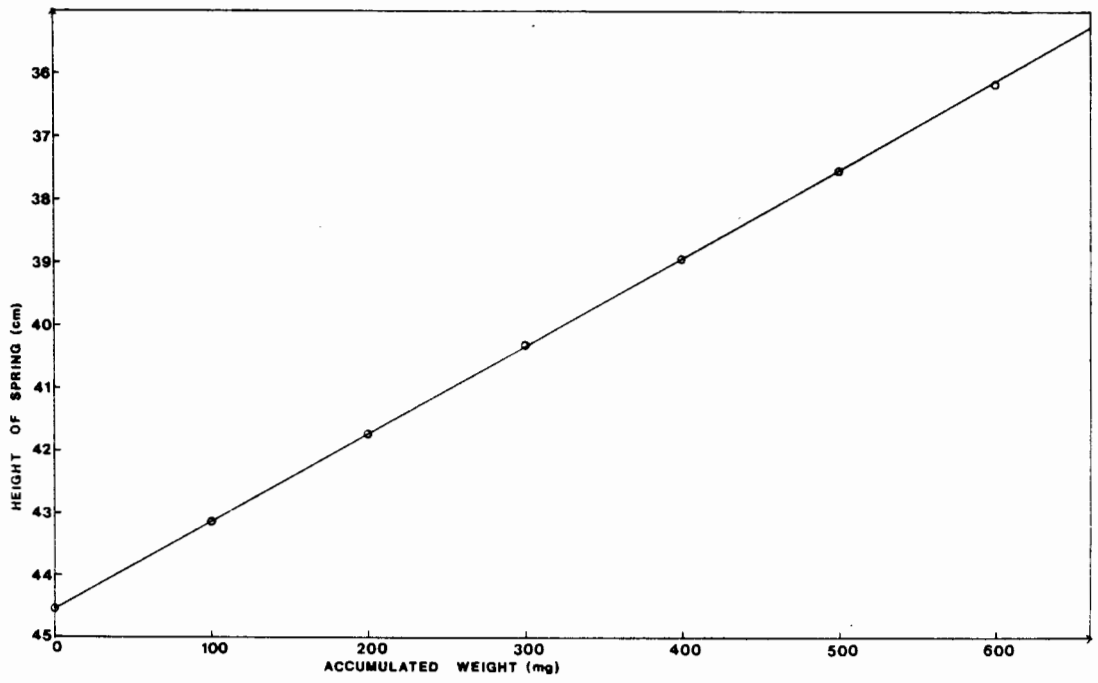


Figure 5.2 Calibration Curve of the Spring

5.2.1 Experiment A

Clathrate crystals of $Ni(NCS)_2(3\text{-}MePy)_4.ChCl_3$ were crystallized by the same procedure described in Chapter 4. Microanalysis of percentage carbon, hydrogen and nitrogen content confirmed a 1:1 molar ratio of host to guest.

354.3mg (0.00053 mol) of clathrate crystals were weighed out, after being carefully dabbed dry from mother liquor and placed into the basket of the McBain balance. The system was evacuated, the pressure being held constant at 77.75 mmHg, and the temperature gradually raised to 61°C. The height of the spring was read through the travelling telescope every five minutes, and a graph of height versus time plotted to follow the desorption process. When the graph (figure 5.3) levelled off, it was a clear indication that all the guest had been desorbed. From the difference in height, weight loss of sample could be evaluated.

Percentage carbon, hydrogen and nitrogen content were determined by microanalysis after guest desorption, providing a stoicheiometric evaluation of guest content. Powder photographs were taken, using extra sample in the tube, before evacuation, during evacuation and after complete guest desorption.

Results

Refer to Figure 5.3

(a) The sample was weighed at the end of the experiment.
Mass loss = 66.3 mg (0.00053 mol chloroform)
Assuming a 1:1 host:guest molar ratio, the theoretical mass loss due to chloroform = 63.4 mg (0.00033 mol). Thus, ratio of host: guest = 1:1.04(1)

(b) From the calibration curve (conditions in vacuo)
Height difference = 0.873 cm
= 62.4 mg (0.00052 mol) chloroform

Assuming a 1:1 host:guest molar ratio, the theoretical mass loss of chloroform from the calibration curve = 62.6 mg (0.00052 mol). Thus the ratio of host:guest = 1:0.997(10)

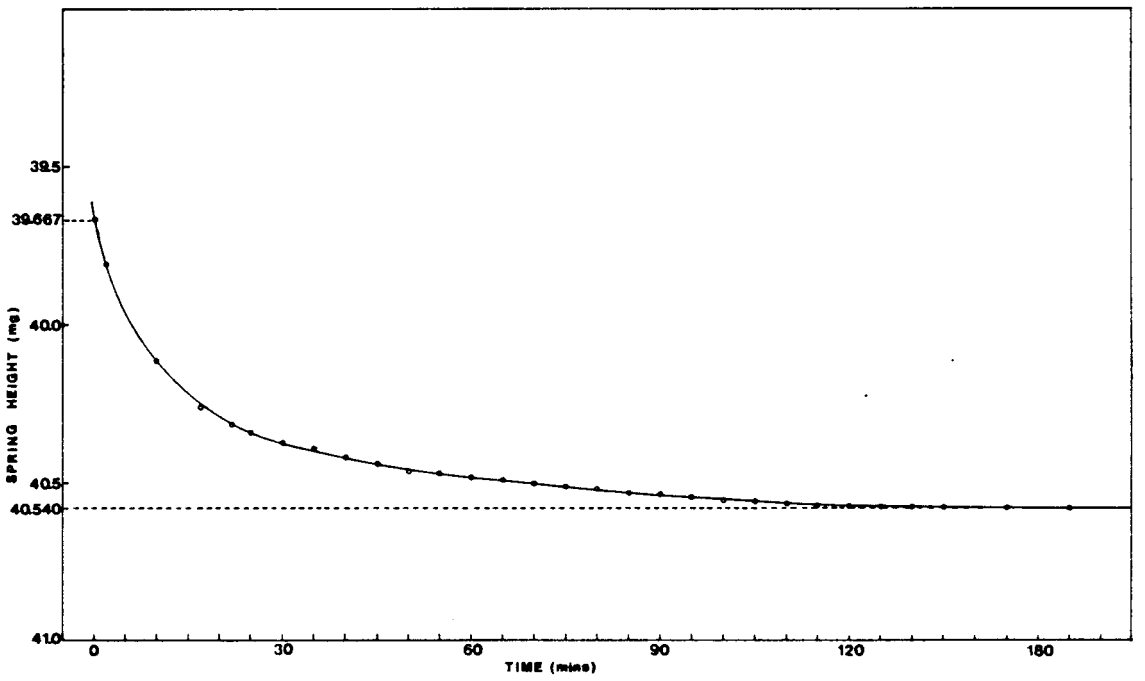


Figure 5.3 The Desorption of Chloroform from the Clathrate $Ni(NCS)_2(3\text{-}MePy)_4.CHCl_3$

Microanalysis

	%C	%H	%N	Host:Guest ratio
(i) Before evacuation	48.85	4.25	12.65	1:1
1:1 structure (theor.)	48.60	4.30	12.60	
(ii) After guest desorption	56.00	5.10	15.45	1:0
"Empty" structure (theor.)	57.00	5.20	15.40	

Powder Photographs

The diffractograms of the three stages appear in Figure 5.4 and the interplanar distances of the more prominent reflections tabulated are below.

TABLE 5.2

INTERPLANAR DISTANCES FOR THE MORE PROMINENT REFLECTIONS WITH RELATIVE INTENSITIES IN PARANTHESIS

Before Evacuation	During guest desorption	After complete guest desorption
d_{exp}	d_{exp}	d_{exp}
8.31 (vs)	8.31 (vs)	8.23 (vs)
6.63 (m)	6.73 (w)	6.73 (w)
5.42 (m)	5.34 (m)	5.34 (m)
4.60 (w)	4.59 (w)	4.58 (w)
4.12 (s)	4.13 (s)	4.15 (s)
3.76 (mw)	3.75 (w)	3.75 (w)
3.44 (w)	3.45 (w)	3.47 (w)
3.16 (vw)	3.17 (w)	3.15 (w)

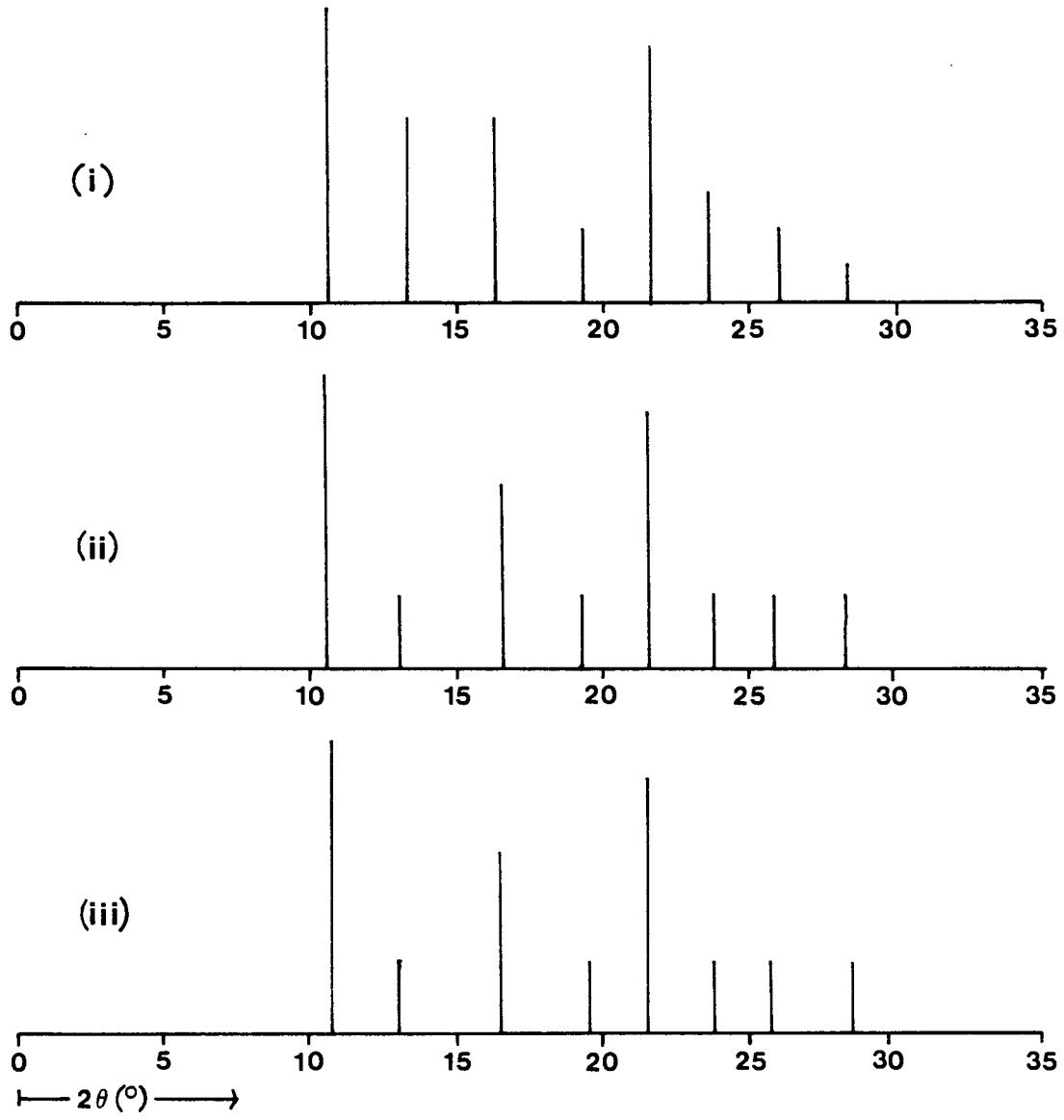


Figure 5.4 X-ray Powder Diffractograms of $Ni(NCS)_2(3\text{-}MePy)_4.CHCl_3$

(i) before guest desorption, (ii) during guest desorption, and (iii) after guest desorption, showing relative intensities of the powder lines

Conclusion

Interplanar distances at the three stages of the experiment were identical. The reflections causing the boldest lines are those to be considered as being the most important.

The clathrating β-phase structure of $Ni(NCS)_2(3\text{-}MePy)_4$ desorbs its guest molecule, chloroform, at a constant rate ($\beta_1 \rightarrow \beta_0$), and in so doing, retains its rigid molecular framework.

5.2.2 Experiment B

An interesting observation was made when trying to form $Ni(NCS)_2(3\text{-}MePy)_4.CHCl_3$ crystals by dissolving the host complex in chloroform alone. Microanalysis of the resultant crystals showed that the guest was included in a ratio of between 1:1.5 and 1:2 of host:guest.

	%C	%H	%N
Theoretical 1:2	42.70	3.80	10.70
Sample 1	42.40	3.80	9.0
Sample 2	42.95	3.85	11.05

The crystals formed in masses, too indistinctly for single crystals to be selected for X-ray crystal structure determination.

351.3 mg of the crystals were placed into the basket of the McBain balance. The system was evacuated to a pressure of 77.75 mmHg and the temperature gradually raised to 40°C. Guest loss was monitored by plotting height of the spring versus time. The plot took the same shape as Figure 5.3

Guest desorption was slow - only after ten days did the graph level out.

Results

a) The sample was weighed after complete guest desorption
Mass loss = 97.7 mg (0.00082 mol) chloroform
Assuming a 1: host:guest molar ratio, the theoretical mass loss due to chloroform = 62.9 mg (0.00053 mol). Thus the ratio of host:guest = 1:1.55(1)

b) From the calibration curve (conditions in vacuo)
Height difference = 1.435 cm
= 102.6 mg (0.00086 mol) chloroform
Assuming a 1:1 host:guest molar ratio, the theoretical mass loss of chloroform read off the calibration curve, corresponding to the mass of the sample used = 62.9 mg (0.00053 mol) chloroform. Thus the ratio of host:guest = 1:1.63(2)

Microanalysis

		%C	%H	%N	Host:Guest ratio
(i)	Before evacuation	44.90	4.05	11.50	1:1.54*
	Theoretical 1:2	42.70	3.80	10.70	
(ii)	After guest desorption	54.30	5.00	14.75	1:0.19
	"Empty" cage (theor.)	57.00	5.20	15.40	

* This result is lower than the expected 1:2 for this particular clathrate. The deviation may be attributed to initial rapid escape of chloroform from the host lattice, during weighing and handling.

Powder Photographs

X-ray powder photographs were taken before evacuation and after guest desorption the interplanar distances, d_{exp}, were calculated and tabulated below. The diffractograms appear in Figure 5.5

TABLE 5.3

INTERPLANAR DISTANCES FOR THE MORE PROMINENT REFLECTIONS WITH RELATIVE INTENSITIES IN PARENTHESES

Before evacuation d_{exp}	After guest desorption d_{exp}
8.29 (vs)	8.35 (vs)
6.78 (mw)	6.56 (w)
5.28 (m)	5.40 (m)
4.59 (w)	4.59 (w)
4.10 (s)	4.15 (s)
3.77 (mw)	3.78 (w)
3.43 (w)	3.44 (w)
3.22 (w)	3.20 (w)

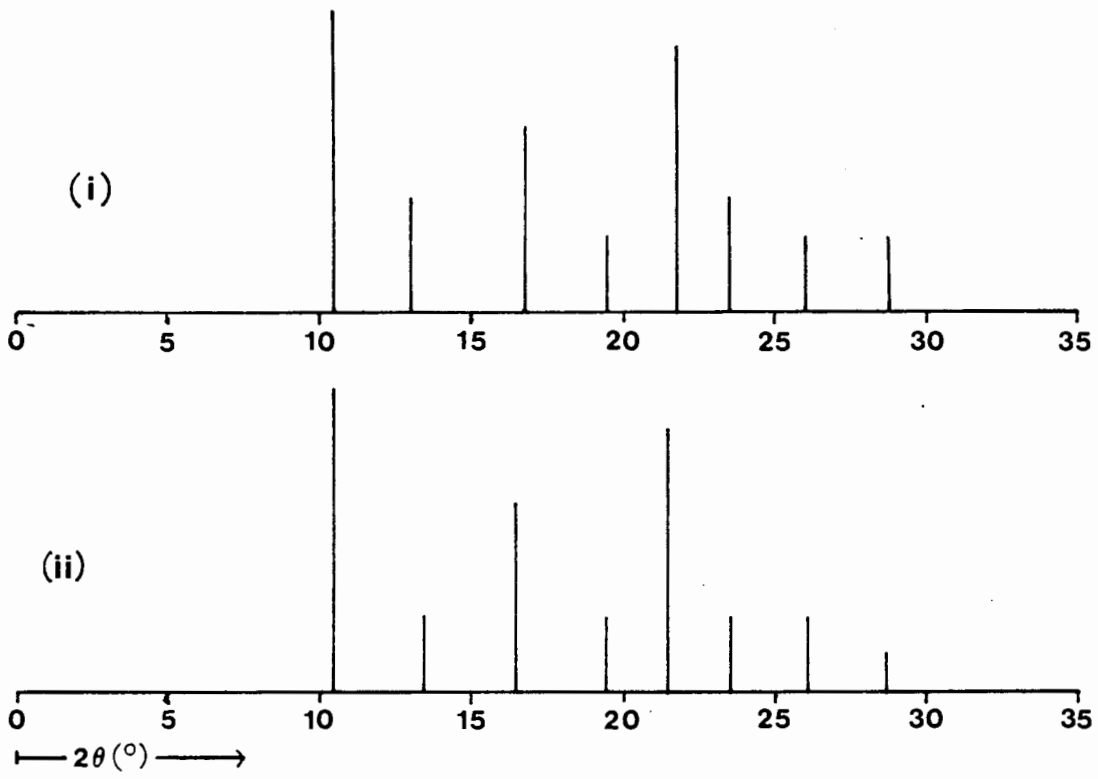


Figure 5.5 X-ray Powder Diffractograms of Experiment B,

(i) before evacuation

(ii) after guest desorption

Conclusion

Interplanar distances for the most prominent reflections are the same. The β- phase structure of these clathrate crystals has not broken down during desorption of the guest over such a long time (10 days). A small fraction of chloroform (0.19) still seems to occupy the voids in the host lattice. Thus the crystal framework is a relatively stable one.

Furthermore, the reflections in this experiment correspond both in magnitude of interplanar distance and in intensity to those in Experiment A. In other words, the molecular structure which crystallizes from solution where two guests, p-Xylene and chloroform, compete is identical to that formed when the host complex is crystallized from chloroform alone.

CHAPTER 6

CHAPTER 6

A POTENTIAL ENERGY STUDY OF THE DIMETHYLSULPHOXIDE AND CHLOROFORM CLATHRATES

6.1 INTRODUCTION

The ligands of the host complexes of clathrate compounds have a great versatility in their conformational flexibility. This conformational freedom of the pyridine rings is an important factor in the shaping of the cavities and in the clathration of guest molecules of different shapes and sizes.

By measuring the non-bonded interaction energies we obtain an idea of the potential energy environment in the voids formed in the molecular framework by the host molecules, and can predict what shape the empty layers, channels or cages will take. The potential energy consists of many terms, the most important being van der Waals, torsional, coulombic, dipole-dipole, ion-dipole, hydrogen bonding and charge transfer energies [73]. Undoubtedly it is the van der Waals energy, arising from dispersion and exchange repulsive terms, which plays the leading role in clathrate systems.

Semi-empirical potential functions describing van der Waals interactions between pairs of non-bonded atoms have been used in the study of the conformational stability of clathrates [74]. The atom-pair potential curves are expressed as

$$V(r) = \frac{ae^{-br} - cr^{-6}}{r^{d}}$$

where r (in $\mathring{A}$) stands for the interatomic distance, and a, b, c and d are empirical parameters assumed in the calculation, quite often varying from author to author.

It is assumed that the overall conformation of the complex is determined by the sum of the interactions of all neighbouring groups. The energy summation may be made for both inter- and intra-molecular interactions. Thus, the results obtained from the potential functions serve merely as an estimate of the true non-bonded intramolecular energies in the crystals. Only qualitative agreement can be reached, not quantitative since the assumptions made in the theory are inadequate. The assumptions are that there is no bond stretching, no bond angle expansion and that there are no residual partial charges.

So, what we would like to interpret in the present study is the shape of the channel and where about in the channel the guests are likely to settle. By moving a guest along a channel the potential energy can be computed at any chosen location. The outward passage of the guest will be opposed by the repulsive forces when any two atoms approach each other closer than the equilibrium distances. This process of escape can be regarded as a dissociation reaction in which the rate of reaction depends on the activation energy.

Powell[4] defines this activation energy as "a measure of the work required to bring the enclosed molecule to the middle of an exit hole from which it may pass with equal ease into or out of the case."

The potential energy program EENY, written by Motherwell[48], was used in the calculations with constants described by Giglio [75] and Fedeli et al [76].

All input data for the geometry of the host molecules were taken from the final refined least-squares cycles of each structure.

6.2 AN ENERGY STUDY OF THE DIMETHYLSULPHOXIDE CLATHRATE

Looking at the molecular packing down the Z axis (Figure 3.7), it is observed that there are two non-equivalent rhomboidal-shaped voids, in each of which are located four guest molecules. These voids represent channels running parallel to the Z axis. The aim of this investigation is to find out what shape these channels take and how the guest molecules fit into them. Furthermore each channel is divided into two sub-channels, each accommodating two guest molecules.

To determine the minima in the energy profiles, potential energy measurements were taken across the unit cell at different levels. The energy profile along each channel was evaluated, and subsequently the potential energies of the sub-channels relative to each other. This results in the study of guest-guest interactions[25].

(a) Energy Map

The whole unit cell was scanned in steps of 1.26Å along X and 0.61Å along Y, every 0.51Å along Z. Intermolecular interactions were calculated between the host molecules in all the symmetry related positions surrounding the unit cell, and an arbitrary methyl group starting at x = 0, y = 0, z = 0. All energies less than 20 kcal mol^{-1} were plotted.

Twenty two-dimensional energy maps were evaluated, effectively scanning the energy profile of each entire channel. Each two-dimensional map was contoured at 10 kcal intervals, and it was found that the positions of lowest energy corresponded closely to the location of the guest molecules found by the structure analysis. These maps are shown in sequence in Figure 6.1.

A perspective diagram (Figure 6.2) was drawn using the program PLUTO by plotting the outermost ring from each layer. Both channels were plotted, one with central axis at 0.5, 0.5, z, and the other at 1.0, 0.5, z, and viewed relative to the two host molecules that occupy the unit cell.

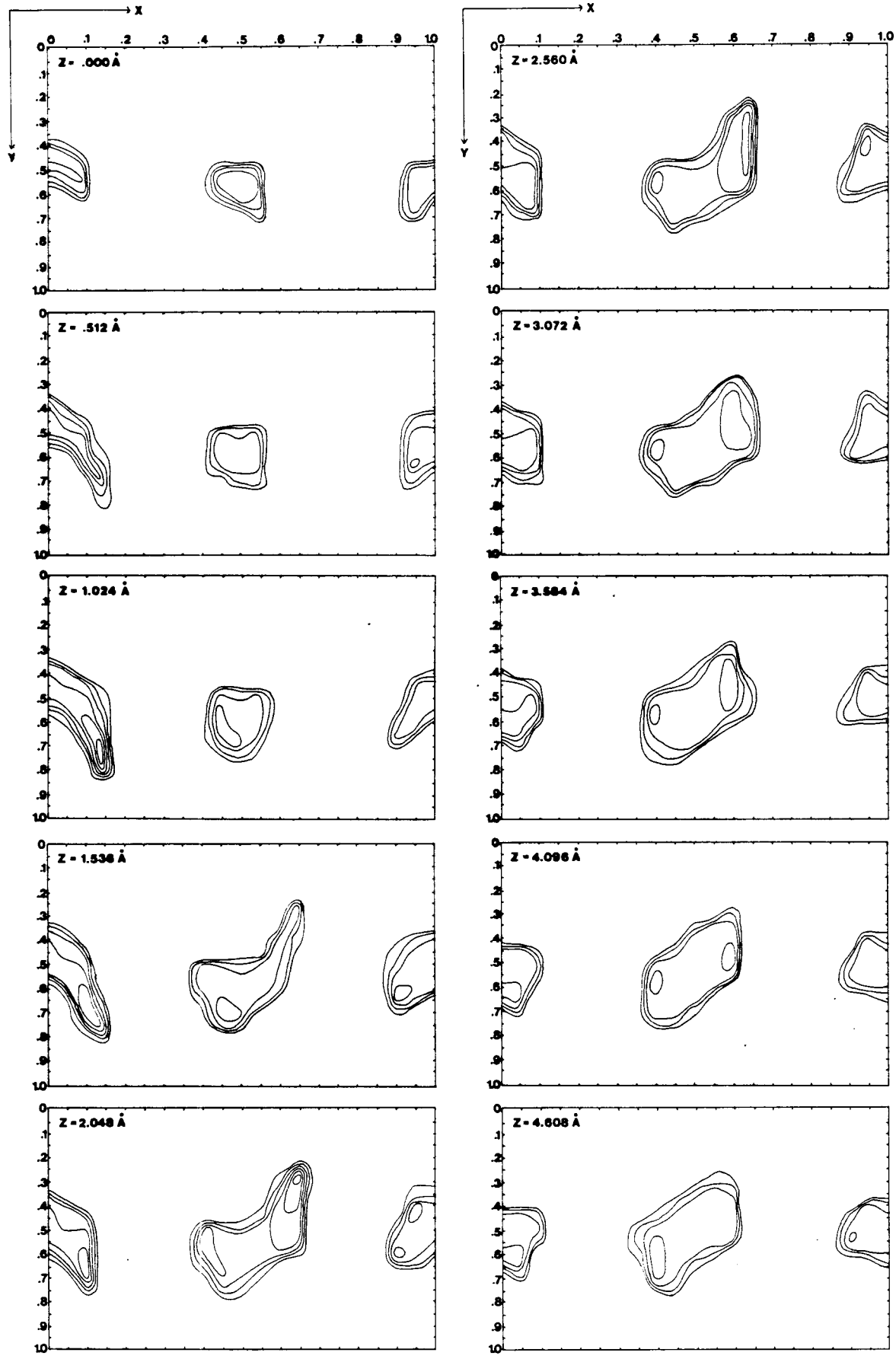


Figure 6.1 Potential Energy Contour Maps of the whole Unit Cell taken every 0.51Å along Z (at 10 kcal intervals)

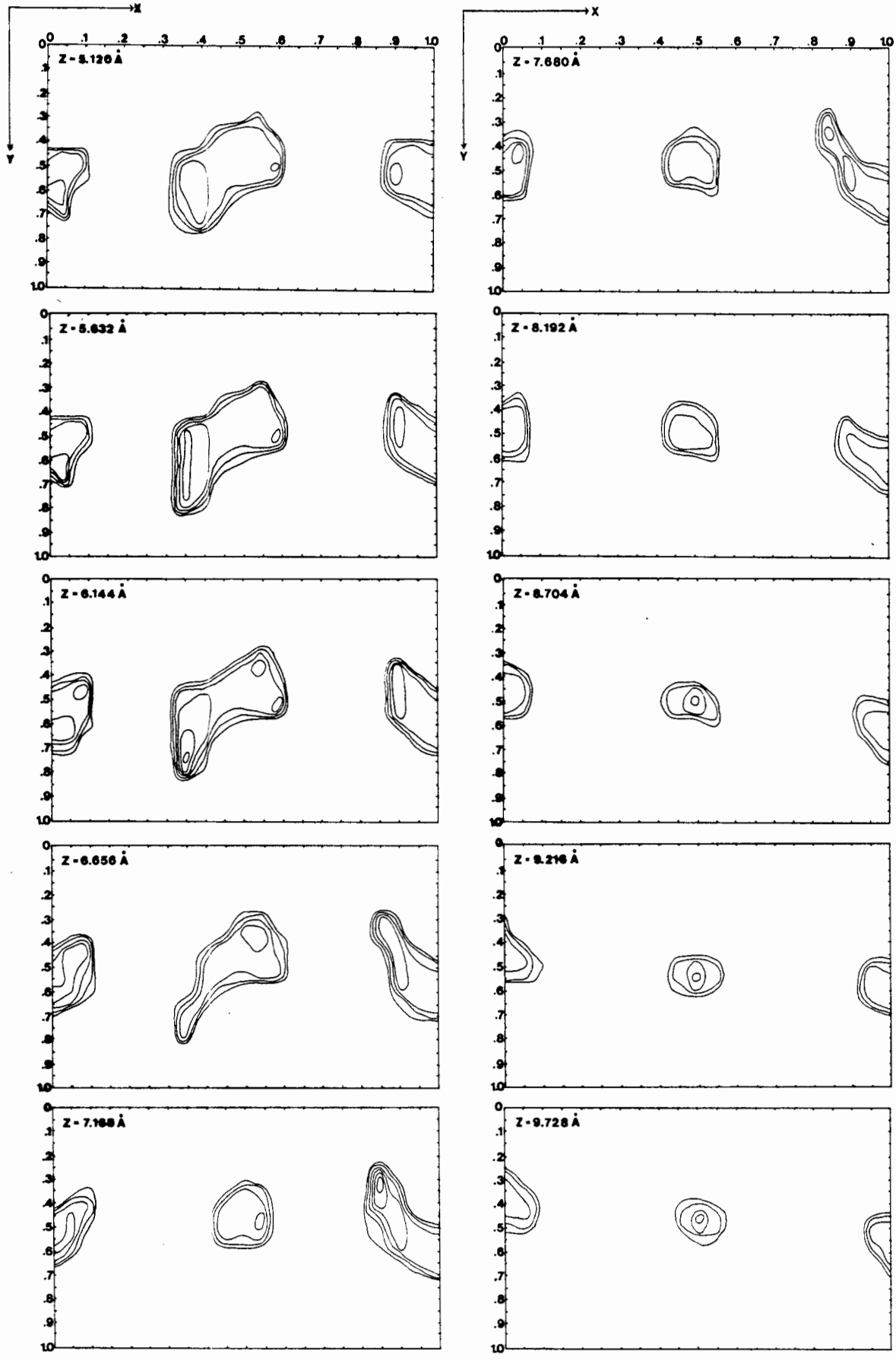


Figure 6.1 Continued

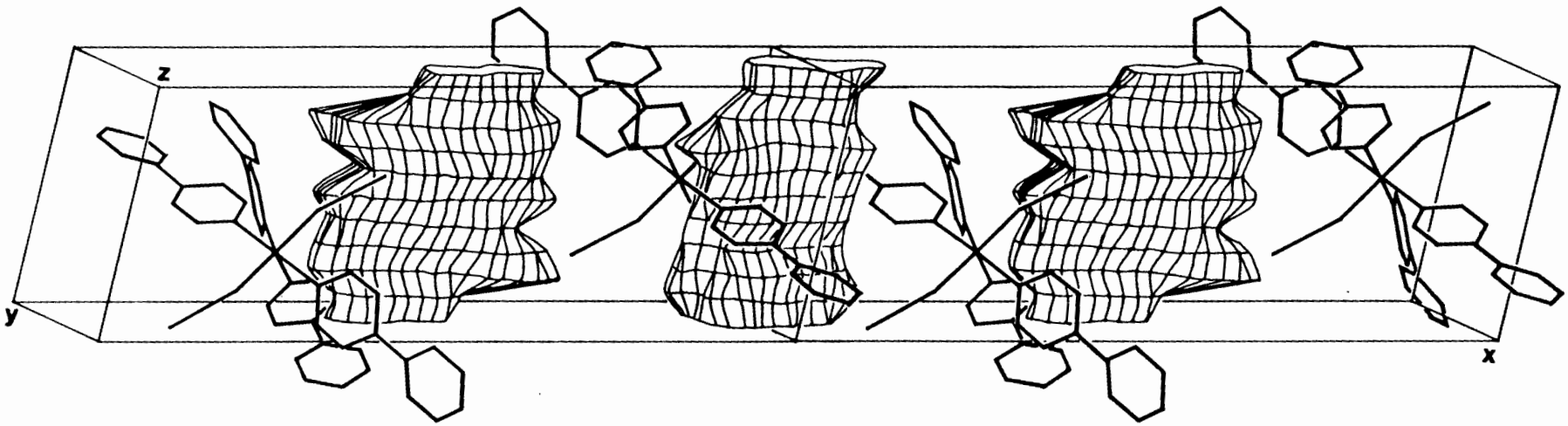


Figure 6.2 Two Unit Cells depicting only the Host Molecules surrounding potential Energy Channels I and II. Channel I is shown at 0.5, 0.5, z and 1.5, 0.5, z and Channel II at 1.0, 0.5, z

Two protrusions are observed in Channel I, positioned across each other diagonally, where steric and non-bonded intermolecular interactions are the lowest, and it is in fact in these positions that two of the DMSO molecules are located, namely S(60) at 0.4001, 0.6085, 0.7911, and its symmetry-generated partner S'(60) at 0.5999, 0.3915, 0.2089.

(b) Single Channel

I Channel I

Figure 6.3 is an illustration of two unit cells viewed down the Y axis, showing the two channels running down the unit cell parallel to the Z axis. Surrounding the channels are the translatory sites of all host molecules which are in such close proximity to the channels that non-bonded interactions will be significant. Host molecules are defined by the notation (n, t_x, t_y, t_z) where n is the symmetry operator and t_x, t_y, t_z the unit cell translations. In the present space group, n = 1 defines symmetry x, y, z and n = 2 defines -x, -y, -z. The host lattice was kept rigid in all the following calculations.

A. Single Methyl Group as a Probe

A single methyl(ME) group was placed in the centre of Channel I, at position 0.5, 0.5, 0.0 and the non-bonded interactions calculated. The energy sum was -3.1 kcal. There were no "close contacts" between guest and host molecules. The methyl group was translated by 0.51Å along Z : close contact between ME and H(112) was negligible (0.1 kcal) and the energy sum totalled -2.8 kcal. As the methyl group was translated by 0.51Å at a time through the whole unit cell the energy sum did not change significantly. Results are tabulated in Table 6.1 but have not been represented graphically.

Quite clearly the guest is far too small for any non-bonded interactions to come into play, and such a system would be completely unfavourable when considering a "stable" clathrate system, where guest-host van der Waals forces are important. Here the guest encounters no energy barrier and diffuses freely through the channel.

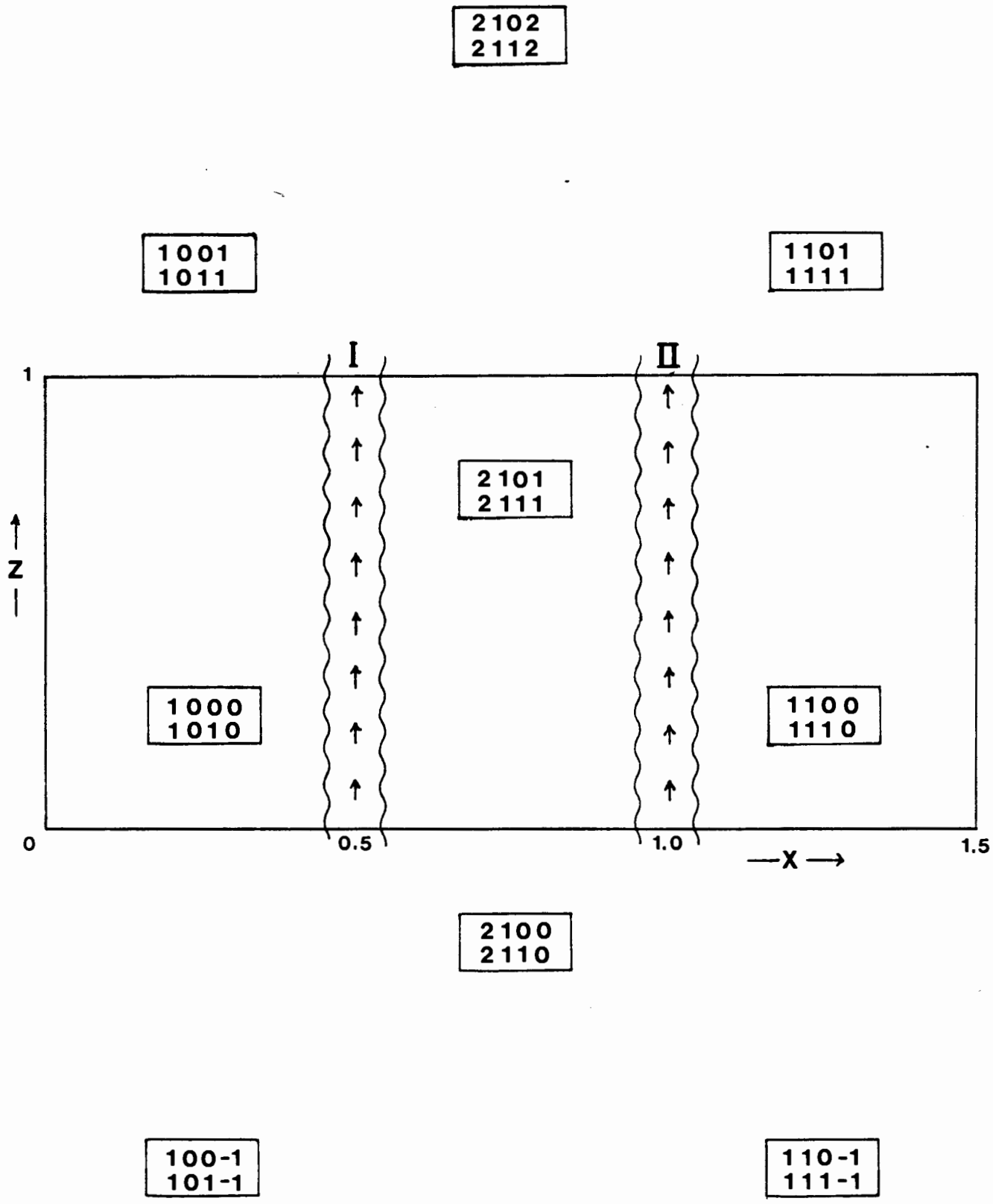


Figure 6.3 The Translation of DMSO through Channels I and II

B. Whole DMSO Molecule in Channel

A whole DMSO molecule was placed in the centre of the channel, in an arbitrary orientation. Its fractional atomic coordinates were calculated from the average bond lengths and angles derived in the final refinement of the structure. These coordinates are:

Sulphur	0.5000, 0.5000, 0.0000
Oxygen	0.5000, 0.3884, -0.1071
Methyl 1	0.4448, 0.5830, -0.0049
Methyl 2	0.5552, 0.5761, -0.0359

The energy sum was 4.5 kcal, due to close contacts arising between the guest molecule and the closest host molecules, at 1000, 1010, 2100 and 2110. As the guest was translated through the cell along Z by 0.51Å at a time, the energy sum increased until an energy barrier was reached, after which the values decreased. Results are listed in Table 6.1 and depicted in Graph 1 in Figure 6.4.

Larger energy sum values are indicative of host-guest repulsion due to the proximity of the two, and low energy values favour the guest location in the very centre of the cell at 0.5, 0.5, 0.5 (Energy sum = -6.0(2) kcal).

C. DMSO molecule allowed Rotational Freedom

Still keeping the host lattice rigid, the DMSO molecule was allowed variation in its rotational parameters (φ , θ , ψ) in order to find a minimum in the energy profile at each translatory site along the Z axis. Results are tabulated in Table 6.1 and represented by Graph 2 in Figure 6.4.

Not only was there a decrease in energy at the 0.5, 0.5, 0.5 position (to -7.7 kcal) but also in the energy barriers encountered at z = 0.2 and 0.9. Thus this model involving guest rotational freedom demonstrates the ease with which the guest is able to orientate itself to minimise the energy profile as it is translated through the cell.

TABLE 6.1

NON-BONDED INTERACTIONS FOR SINGLE CHANNEL I

Position	Energy Sum (kcal)		
	A	B	C
0.5, 0.5, 0.0	-3.1	4.5	-9.0
0.5, 0.5, 0.1	-2.8	20.7	-8.7
0.5, 0.5, 0.2	-2.3	62.0	-3.5
0.5, 0.5, 0.3	-2.2	43.8	-7.9
0.5, 0.5, 0.4	-2.1	2.4	-7.4
0.5, 0.5, 0.5	-2.0	-6.3	-7.7
0.5, 0.5, 0.6	-2.1	-5.8	-7.8
0.5, 0.5, 0.7	-2.2	0.2	-7.2
0.5, 0.5, 0.8	-2.3	2.1	-8.5
0.5, 0.5, 0.9	-2.8	0.4	-0.7
0.5, 0.5, 1.0	-3.1	4.5	-9.2

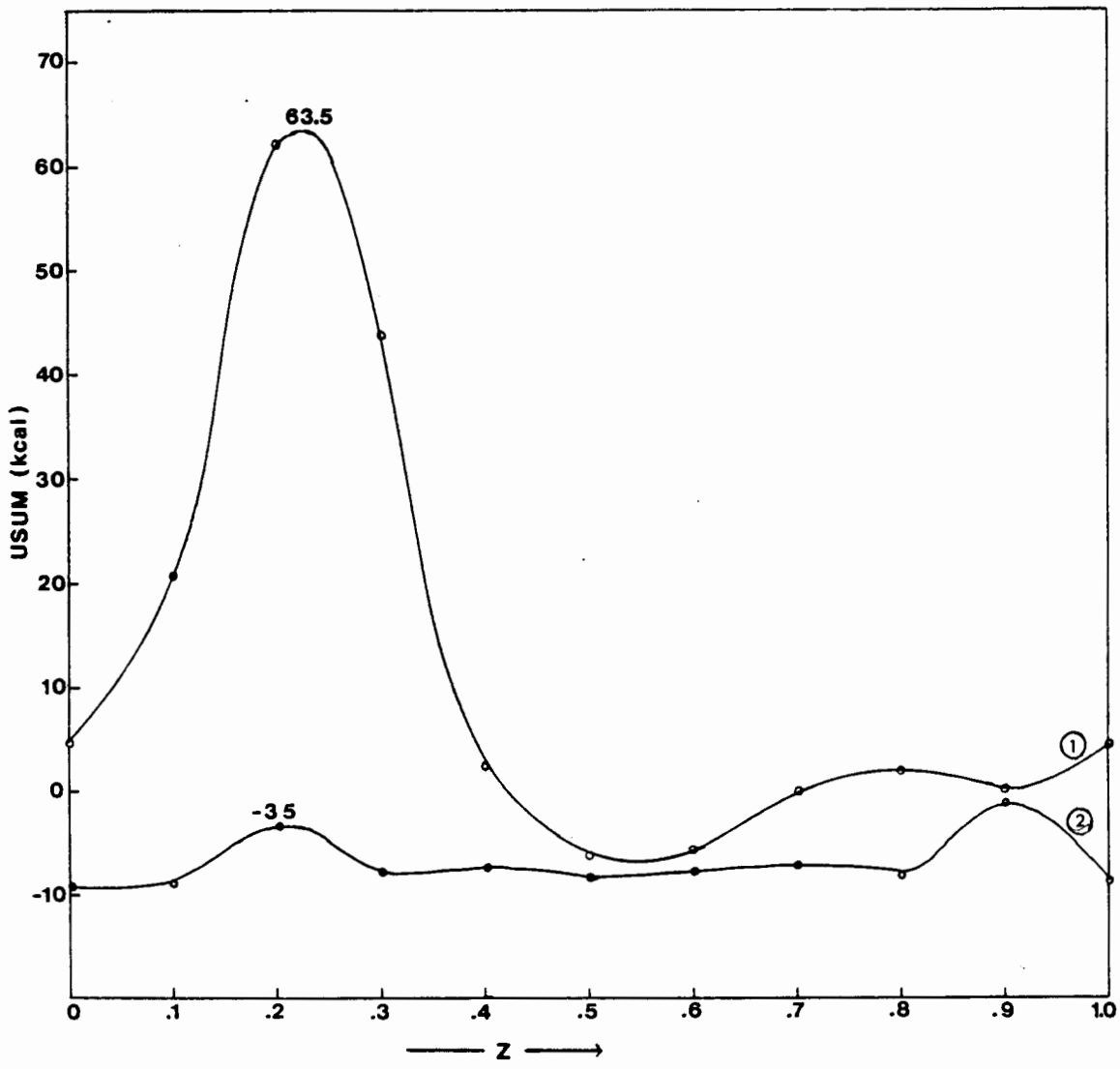


Figure 6.4 Non-bonded potential energies (USUM) plotted at each translatory position along Z (Channel I)

II Channel II

A. Whole DMSO Molecule (Rigid)

The potential energy calculations were repeated, with the DMSO molecule situated in the centre of Channel II, its atomic coordinates being:

Sulphur	1.0000, 0.5000, 0.0000
Oxygen	1.0000, 0.3884, -0.1071
Methyl 1	0.9448, 0.5830, -0.0049
Methyl 2	1.0552, 0.5761, -0.0359

The host lattice was again held rigid throughout.

The guest molecule was held rigid and the non-bonded interactions calculated at the ten translatory sites through the channel along the Z axis. Results appear in Table 6.2 and in Figure 6.5, Graph 1.

The energies are notably lower than the corresponding energies found for translation through Channel I. An energy barrier is encountered at position 0.0, 0.5, 0.85 (energy sum $\approx$16.0 kcal), indicating that the guest is effectively trapped at this site. This value is significantly lower than the corresponding energy maximum achieved in Channel I, namely 62.0 kcal. Host-guest interactions and van der Waals forces seem to be weaker in Channel II, "binding" the guest molecule less effectively than in Channel I. Consequently, the guest molecule can dissociate itself from the crystal lattice far more easily in this channel.

B. Whole DMSO Molecule (Rotating)

The calculations were repeated, this time allowing the DMSO molecule rotational freedom. Results, listed in Table 6.2 and represented by Graph 2 (Figure 6.5), show that no significant energy barrier was encountered. The DMSO molecule can therefore diffuse through this channel with ease.

TABLE 6.2

NON-BONDED INTERACTIONS FOR SINGLE CHANNEL II

Position	Energy Sum (kcal)	
	A	B
1.0, 0.5, 0.0	-2.4	-8.5
1.0, 0.5, 0.1	-7.8	-9.1
1.0, 0.5, 0.2	-6.2	-6.9
1.0, 0.5, 0.3	-4.0	-6.3
1.0, 0.5, 0.4	-4.0	-7.7
1.0, 0.5, 0.5	-6.3	-8.5
1.0, 0.5, 0.6	-6.7	-8.2
1.0, 0.5, 0.7	-1.5	-7.9
1.0, 0.5, 0.8	12.7	-6.9
1.0, 0.5, 0.9	16.0	-7.4
1.0, 0.5, 1.0	-2.4	-8.5

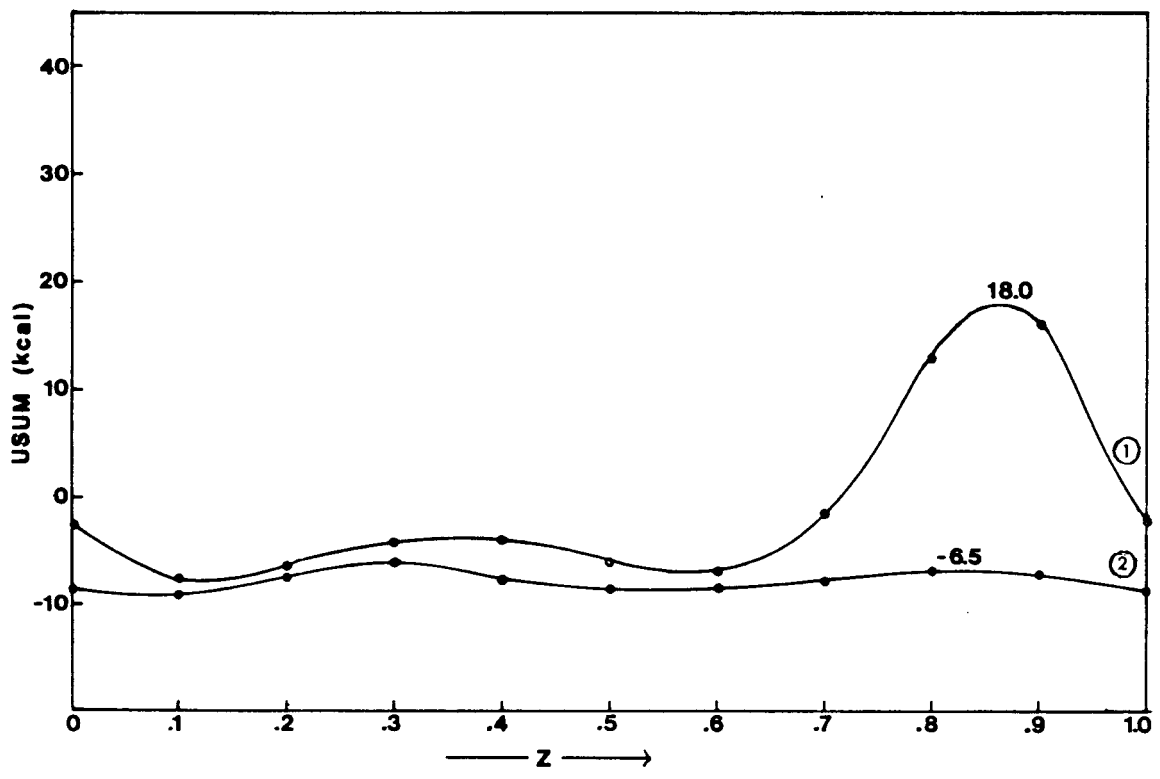


Figure 6.5 Non-bonded potential energies (USUM) plotted at each translatory position along Z (Channel II).

C. Double Channel

From the crystallographic molecular packing, two different voids are formed which represent two non-identical channels. However, on closer inspection of each channel individually it seems that the four guest molecules located therein are positioned in groups of two along the Z axis. This gives the impression that there are two sub-channels within each channel, each housing two DMSO molecules.

For the purpose of this potential energy study, we have placed one guest molecule in each sub-channel, and have attempted to simulate independent movement of the two (call them Guest 1 and Guest 2) in a given double channel. In this manner we hoped to find more than one energy minimum in the energy profiles of the channels, indicating the positions where the four guests are most likely to be situated.

Figure 6.6 diagramatically represents the double channels and the host molecules involved in the potential energy determinations.

We were presented with two problems which required certain adjustments to the mode of calculation:

a) $P\bar{1}$ symmetry produced symmetrically equivalent guest molecules in opposite sub-channels causing "clash" of the guests and giving unrequired repulsive energies. Thus the sapce group was changed to P1, non-centrosymmetric.

b) The host molecule, treated as P1, consisted of too many atomic positions for the program. Thus, the system was divided into four entities, namely:

Host 1	Located at x, y, z
Host 2	Located at -x, -y, -z
Guest A	Located in Channel IA or IIB
Guest B	Located in Channel IIA or IIB

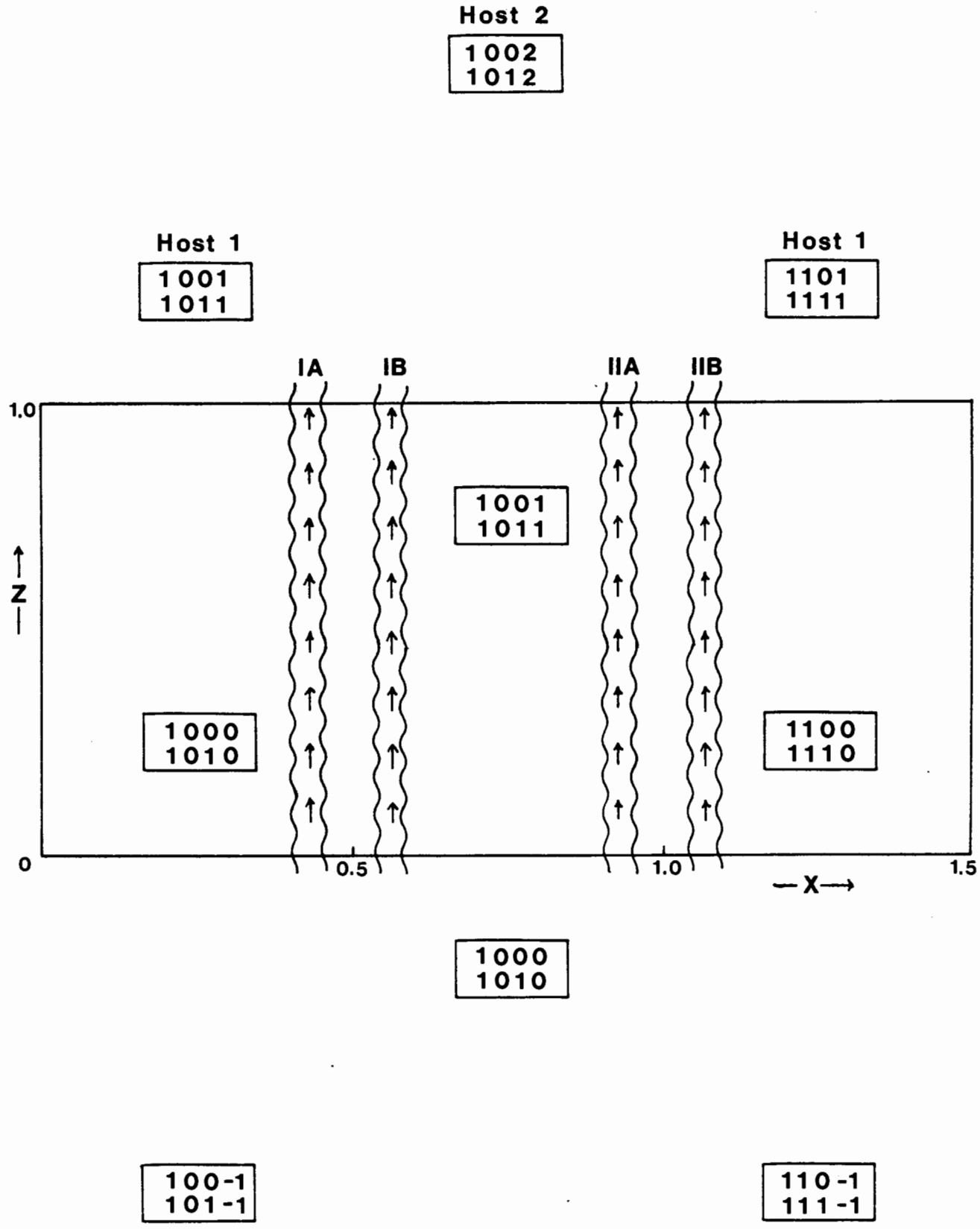

Host 2
1002
1012
Host 1
1001
1011
Host 1
1101
1111
IA
IB
IIA
IIB
1.0
Z
1001
1011
1000
1010
1100
1110
0
0.5
1.0
1.5
X
1000
1010
100-1
101-1
110-1
111-1

Figure 6.6

The total potential energy at any position of Guest A and Guest B is thus the summation of the following non-bonded interaction energies, for each pair (i, j):

Channel I

1) Host 1 ↔ Guest A (z_i) i = 0, 0.1, ..., 1.0
2) Host 2 ↔ Guest A (z_i) i = 0, 0.1, ..., 1.0
3) Host 2 ↔ Guest B (z_j) j = 0, 0.1, ..., 1.0
4) Host 1 + Guest A (z_i) ↔ Guest B (z_j) i, j = 0, 0.1, ..., 1.0

Channel II

1) Host 1 ↔ Guest A (z_i) i = 0, 0.1, ..., 1.0
2) Host 1 ↔ Guest B (z_j) j = 0, 0.1, ..., 1.0
3) Host 2 ↔ Guest A (z_i) i = 0, 0.1, ..., 1.0
4) Host 2 + Guest A (z_i) ↔ Guest B (z_j) i, j = 0, 0.1, ..., 1.0

The host lattice was kept rigid.

The position of the central sulphur atom of dimethylsulphoxide was chosen as the mean position of the two molecules in the sub-channel. The geometry of the molecules in the following orientations determined the coordinates of the oxygen and methyl groups:

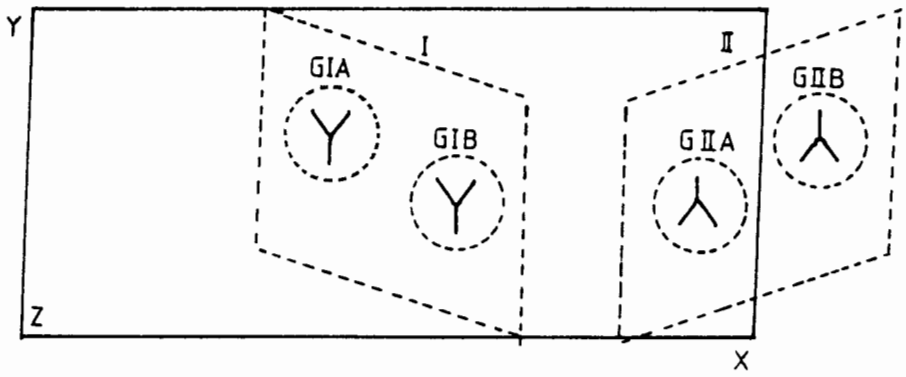


Figure 6.7

The starting coordinates of the four guest molecules are:

	Guest IA			Guest IB		
	x	y	z	x	y	z
Sulphur	0.4190	0.5960	0.0000	0.5810	0.4040	0.0000
Oxygen	0.3638	0.6790	-0.0049	0.5258	0.4870	-0.0049
Methyl 1	0.4742	0.6721	-0.0359	0.6362	0.4801	-0.0359
Methyl 2	0.4190	0.4844	-0.1071	0.5810	0.2924	-0.1071

	Guest IIA			Guest IIB		
	x	y	z	x	y	z
Sulphur	0.9280	0.4000	0.0000	1.0720	0.6000	0.0000
Oxygen	0.9280	0.5116	-0.0059	1.0720	0.4884	-0.0059
Methyl 1	0.8728	0.3239	-0.0771	1.1272	0.6761	-0.0771
Methyl 2	0.9832	0.3170	-0.1080	1.0168	0.6830	-0.1080

These energies were summed and the totals for each (i, j) tabulated. Results appear in Tables 6.3 and 6.4 for Channels I and II respectively.

Energy values are very high, indicating that besides host-guest interactions, guest-guest interactions in this structure play an important role in determining the potential energy environment. Repulsive forces due to steric and dipole-dipole interactions are strong as the two guest molecules come closer to each other, each in its sub-channel. The favourable positions of the DMSO molecules should in fact coincide with the positions determined in the refinement of the structure. Taking the sulphur atom as a reference, the refined z coordinates were:

Channel IA	z = 0.79	Guest IA
	z = 0.32	Guest IA
Channel IB	z = 0.68	Guest IB
	z = 0.21	Guest IB

The potential energy calculations gave energy minima at the following positions (marked with an asterisk):

GIA(i)	GIB(j)	Energy Sum (kcal)
0.4	0.6	94.6
0.6	0.7	20.9
0.7	0.3	-7.4

This latter energy reflects the most stable position in the cell for a DMSO molecule. In fact the area along Z between 0.3 and 0.8 displays the lowest potential energies.

In other words, the areas of local energy minima corresponded well with our predictions that the potential energy of the void is lowest at the positions where the electron density maps revealed the sulphur peaks.

The potential energy values were much lower in Channel II than in Channel I. This is in good agreement with results found in Part (b) of this discussion where DMSO alone was translated through the cell in the centre of the channel.

Electron density maps from the structure determination studies revealed the DMSO molecules lying in the two sub-channels in the following positions:

Channel IIA $z_i = 0.54$
$z_i = 0.08$
Channel IIB $z_j = 0.45$
$z_j = 0.92$

From the table, energy minima are found at positions marked with an asterisk, namely:

GIIA(i)	GIIB(j)	Energy Sum (kcal)
0.1	0.5	95.2
0.2	0.9	92.7
0.6	0.4	20.6
0.6	0.9	21.9

These values are of similar magnitude to those found for Channel I, even though the surrounding molecules display larger repulsive forces in Channel I.

It would have been interesting to apply variation in rotational parameters (ϕ, θ, ψ) to the guest molecules to obtain an understanding on how each molecule could orientate itself at each translatory site, relative to the another in the second sub-channel. However, this study was not pursued owing to the difficulty encountered which necessitated the splitting of energy summations into four separate terms. It could be predicted that an energy barrier would have been encountered, and energy minimum values would have been lower.

We can conclude that the energy model presented here provides a reasonable indication of the environment in the channels. Host molecules cause host-guest repulsion which enforces the guest to lie in selected positions within the channels.

TABLE 6.3

NON-BONDED HOST-GUEST AND GUEST-GUEST INTERACTIONS FOR DOUBLE CHANNEL I

j ⟶

i ↓

GIA \ GIB	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.0	11171.3	2583.3	778.6	684.1	678.4	680.1	686.1	706.7	834.2	2610.3	11171.3
0.1	11470.0	2871.9	1008.7	909.4	903.5	905.2	909.6	915.4	992.7	2804.3	11469.9
0.2	11595.4	3101.9	1201.6	1070.9	1060.1	1061.5	1066.0	1070.3	1132.8	2894.3	11595.3
0.3	10669.5	2211.4	415.8	247.9	205.8	202.3	206.6	210.8	271.8	2018.5	10669.4
0.4	10540.9	2032.7	272.6	209.3	130.0	95.2	94.6*	98.6	159.5	1904.7	10540.8
0.5	10555.1	2032.1	221.8	194.0	219.4	147.4	115.4	114.5	175.2	1920.4	10555.0
0.6	10456.3	1931.8	106.7	28.8	89.6	122.3	53.2	20.9*	76.7	1821.6	10456.2
0.7	10436.4	1912.0	85.3	-7.4*	3.3	71.4	106.9	37.5	62.0	1802.0	10436.3
0.8	10486.3	1961.6	135.0	40.7	36.6	54.6	125.5	160.8	148.1	1856.8	10486.2
0.9	10897.2	2367.6	540.7	446.4	440.8	444.0	464.8	535.6	627.5	2299.0	10897.1
1.0	11171.3	2610.3	778.5	684.0	678.4	680.1	686.1	706.7	834.1	2610.3	11171.2

TABLE 6.4

NON-BONDED HOST-GUEST AND GUEST-GUEST INTERACTIONS FOR DOUBLE CHANNEL II

j ⟶

i ↓ GIIA \ GIIB	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0.0	534.7	1068.6	795.6	406.6	277.3	257.1	263.4	281.0	298.6	333.4	534.7
0.1	234.8	889.4	777.6	293.3	120.5	95.2*	101.3	118.7	132.5	118.9	234.8
0.2	172.9	729.4	738.5	415.2	147.0	78.2	79.2	96.4	110.1	92.7*	172.9
0.3	523.3	1044.1	955.0	752.6	645.6	481.4	438.9	451.0	464.4	446.9	523.3
0.4	311.3	828.2	703.4	402.9	416.6	413.6	275.8	244.3	252.7	234.9	311.2
0.5	105.3	622.1	493.4	157.2	72.8	190.6	213.9	87.1	52.0	29.1	105.1
0.6	92.8	609.6	480.7	140.7	20.6*	40.3	184.3	218.7	88.2	21.9*	92.8
0.7	164.9	681.7	552.9	212.7	88.8	72.7	118.6	273.9	304.5	142.8	170.2
0.8	589.6	1106.4	977.6	637.4	513.3	493.4	503.6	570.1	712.2	711.6	643.7
0.9	598.2	1115.1	986.3	646.1	522.1	502.0	508.4	529.7	583.1	703.3	796.5
1.0	353.4	870.3	741.5	401.3	277.3	257.3	263.5	281.0	298.6	320.7	534.7

6.3 AN ENERGY STUDY OF THE CHLOROFORM CLATHRATE

The molecular packing of the structure was discussed in detail in Section 4.5. In brief, sixteen host molecules are packed in such an arrangement that eight cages connected by channels are formed which run parallel to the X axis, each accommodating two guest molecules.

Figure 4.13 in Chapter 4 indicated the positions of the guests in the cell.

In order to ascertain the nature of the forces holding the guest captive, we need only investigate the potential energy environment of one channel, since all channels are crystallographically equivalent. We therefore studied only the channel whose centre is 0.0, 0.375, 0.375.

The orientation of the guest molecule, chloroform, was chosen from refined positions of Model A. Thus the input data consisted of a central carbon atom and four chlorine atoms forming a tetrahedron. The energy results should be higher since only three chlorines are present in chloroform, but we wished to obtain the maximum possible energy corresponding to the peaks located in the electron density map, even though their site occupancy factor was 0.75.

The shape of the channel is defined by the host molecules directly surrounding it. These are depicted in Figure 6.8. Each host molecule is denoted by (n, t_x, t_y, t_z), n being the symmetry operator and t_x, t_y, t_z the unit cell translations.

The coefficients of the van der Waals potentials were changed to accommodate the chlorine atoms in this model.

A. Single Chlorine Atom as a Probe

The host lattice was kept rigid and a single chlorine atom placed in the centre of the channel. The non-bonded interactions at this point were calculated giving an energy sum of 122.5 kcal, a somewhat high value. We see that close contacts occurred between the chlorine atom and C(17), H(172) and H(173). The atom was translated by 2.63$\mathring{A}$ along

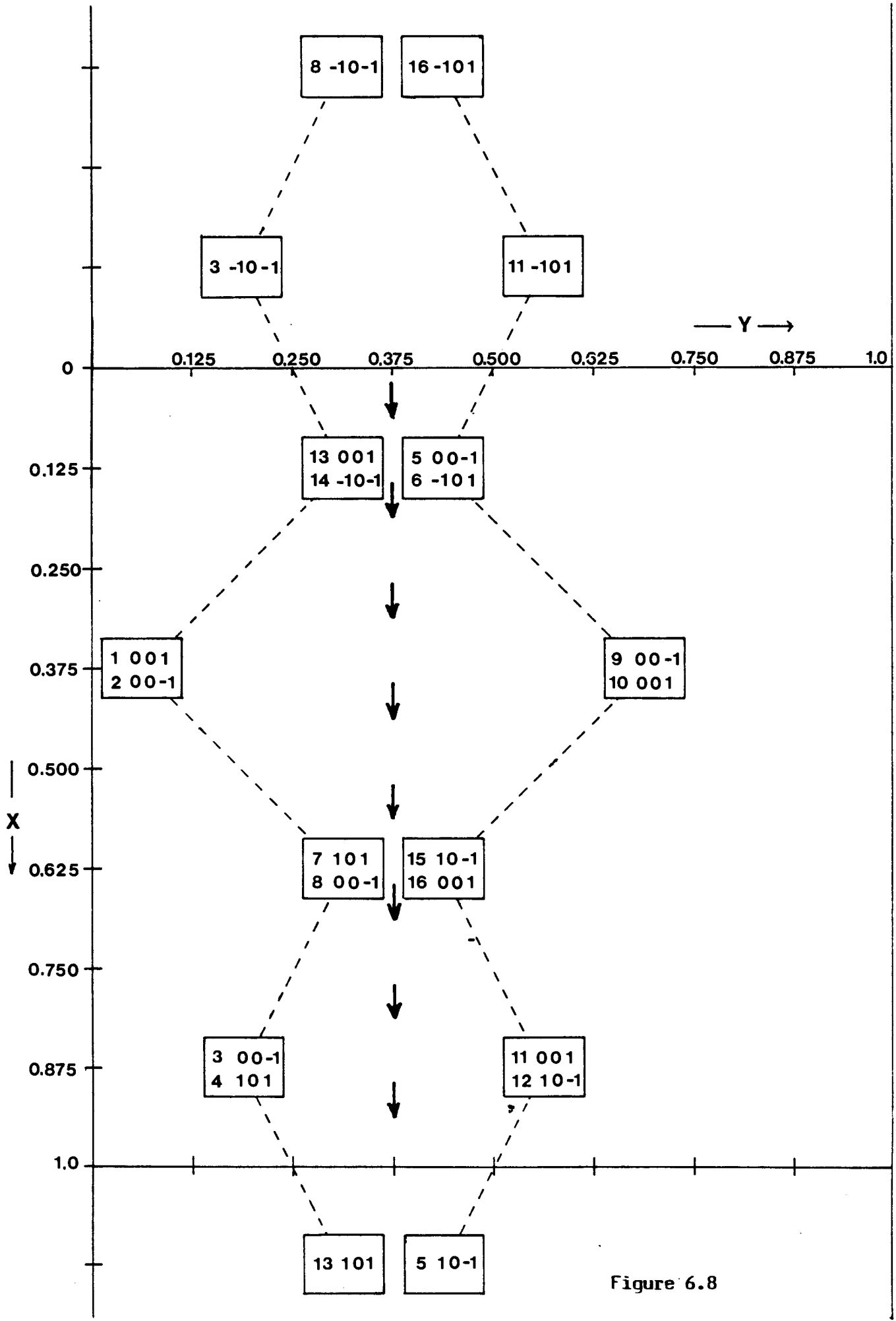

8 -10-1
16 -101
3 -10-1
11 -101
Y
0.125
0.250
0.375
0.500
0.625
0.750
0.875
1.0
0
13 001
14 -10-1
5 00-1
6 -101
1 001
2 00-1
9 00-1
10 001
X
7 101
8 00-1
15 10-1
16 001
3 00-1
4 101
11 001
12 10-1
13 101
5 10-1

Figure 6.8

X and the energy sum was lowered to 2.1 kcal. This position was more favourable. A graph of the energy sums at the ten translatory sites is shown in Figure 6.9 (Graph 1). The results are listed in Table 6.5.

The largest repulsion occurs at x = 0.7 and x = 1.0. Favourable positions for the guest are between x = 0.2 and x = 0.6.

B. Whole Guest Molecule in Centre of Channel

While the host lattice was kept rigid, a whole guest molecule was placed in the centre of the channel. This was effectively a CCl_4 molecule, the four chlorines placed at the corners of a tetrahedron. The following atomic coordinates were used:

C(10)	0.0000, 0.3750, 0.3750
CL(1)	-0.0375, 0.4192, 0.3338
CL(2)	0.0375, 0.3380, 0.3259
CL(3)	0.0375, 0.4120, 0.4241
CL(4)	-0.0375, 0.3308, 0.4163

This guest molecule was translated through the unit cell 2.63Å at a time, and the interactions calculated at each site. The guests in this channel were effectively trapped at the 0.250, 0.375, 0.375 (E = -6.0 kcal) and the 0.500, 0.375, 0.375 (E = -7.4 kcal) sites. (Refer to Graph 2, Figure 6.9). Repulsive forces elsewhere along the channel were excessive, giving very high energy sum results, the greatest repulsion occurring between chlorines and the methyl groups of the pyridine ligands. A smaller energy barrier is encountered at x = 0.4

C. Guest Allowed Rotational Freedom

The model was refined by allowing the guest rotational freedom about ϕ, θ, ψ, at each translatory site along X. Results appear in Table 6.5 and are illustrated by Graph 2 in Figure 6.9.
Here, a lower energy barrier was encountered. The guest molecule was able to orientate itself to negotiate the more exacting apertures of the channel far better. Hence it could find a local minimum in the energy profile in the region between x = 0.25 and 0.50.

D. Host Allowed Conformational Freedom

The model was then adjusted so that the guest molecule remained rigid at each translatory site, while the host lattice was allowed selected conformational freedom. The host molecule (Figure 6.10) was divided into five residues linked by the following four torsion angles:

1	N(2)-Ni(1)-N(11)-C(16)	-31.22°
2	N(1)-Ni(1)-N(21)-C(22)	-37.43°
3	N(2)-Ni(1)-N(31)-C(32)	-36.61°
4	N(1)-Ni(1)-N(41)-C(46)	-34.65°

These were allowed free rotation while the rigid guest molecule moved through the channel. From the results (Table 6.5 and Graph 3, Figure 6.9) one can see that there is a large decrease in the energy barrier encountered. Energy minima now appear at x = 0.0, 0.25 to 0.50, 0.75.

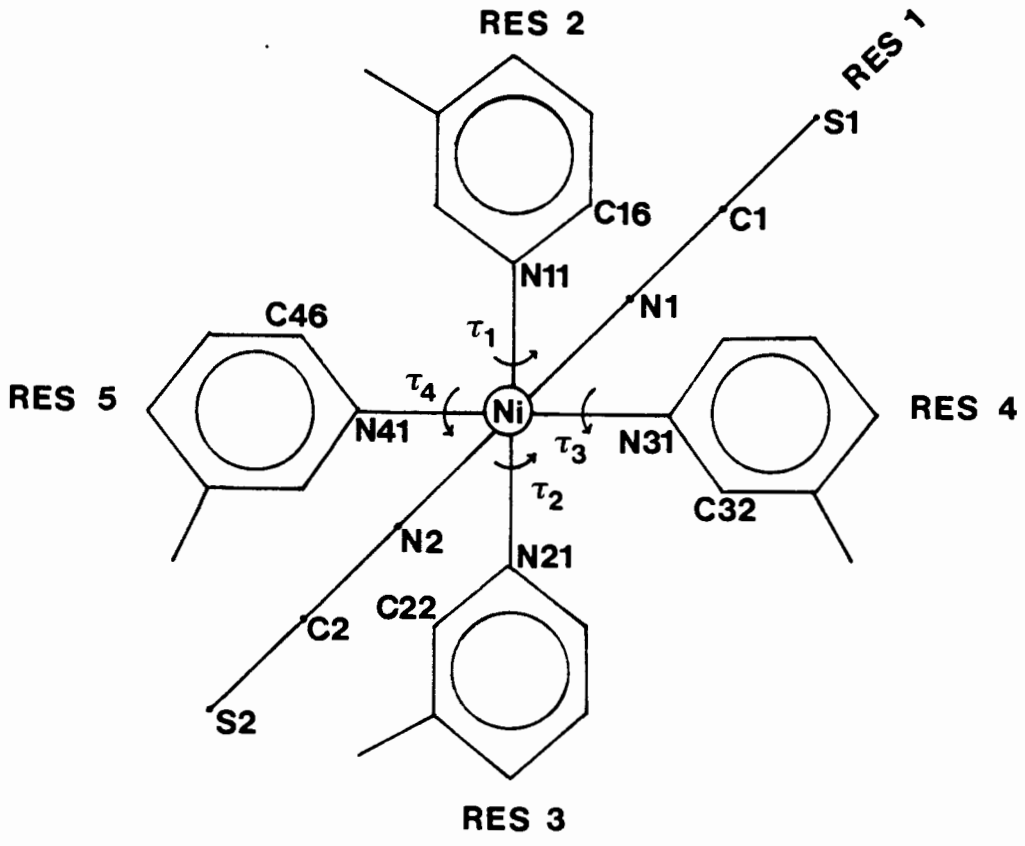


Figure 6.10 The Host Molecule sub-divided into 5 residues linked by 4 torsion angles

E. Both Host Conformational and Guest Rotational Freedom

Finally, the model was adapted to allow both rotational freedom of the guest and host conformational freedom. The energies obtained are tabulated in Table 6.5. There is no change in the energy profile.

TABLE 6.5

NON-BONDED HOST GUEST INTERACTIONS

Position	Energy Sum (kcal)				
	A	B	C	D	E
0.0, 0.375, 0.375	1.9	22.5	22.5	-7.6	-7.6
0.1, 0.375, 0.375	-1.1	2645.7	2645.7	1.2	1.2
0.2, 0.375, 0.375	-1.7	6.4	5.3	4.1	4.1
0.3, 0.375, 0.375	-1.2	-4.8	-4.8	-4.1	-4.1
0.4, 0.375, 0.375	-1.2	18.0	-6.9	-3.1	-3.1
0.5, 0.375, 0.375	-1.3	-7.5	-7.6	-5.8	-5.8
0.6, 0.375, 0.375	-2.2	913.1	4.6	0.8	0.8
0.7, 0.375, 0.375	3.3	457.4	457.4	-6.2	-6.2
0.8, 0.375, 0.375	2.1	229.0	228.5	-5.1	-5.1
0.9, 0.375, 0.375	-1.9	902.7	22.8	1.8	1.8
1.0, 0.375, 0.375	3.4	36.8	36.8	-8.0	-8.0

Conclusion

The energy required to remove the guest (CCl_4) from its case is greatly lowered by allowing conformational fredom of the host molecules. On permitting guest rotational freedom as well, there is no change in the potential energy of the system. Thus it seems that by simply allowing complete conformational freedom, the cavities are able to expand in volulme to accommodate guests at all the possible positions along X, i.e. at x = 0.0, 0.25, 0.50 and 0.75. This situation would be unfavourable since translation throuqh the chnnel would be too easy.

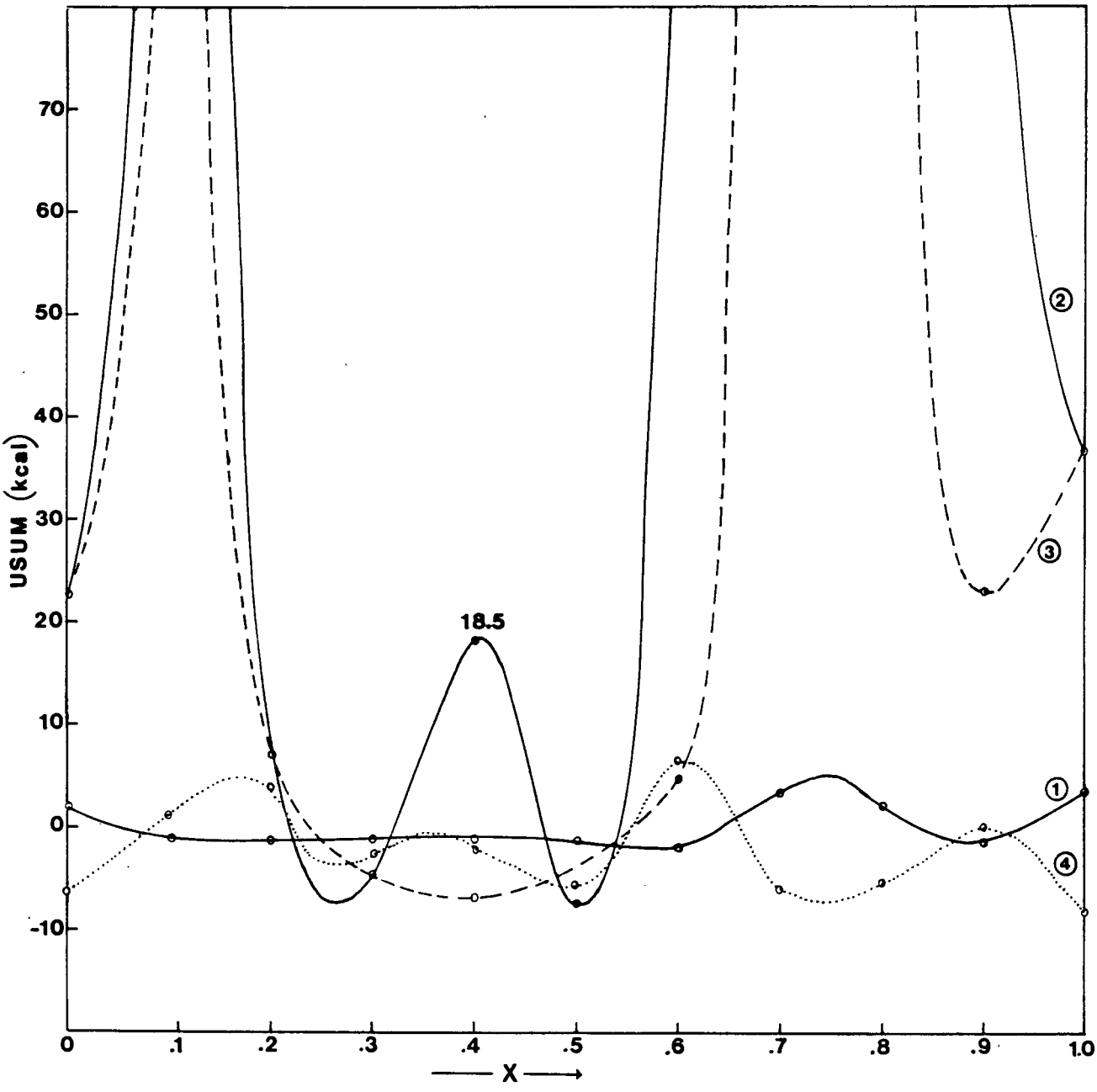


Figure 6.9 Potential Energies (USUM) plotted versus translations of the Guest along the X axis

Hence the best potential energy model in which the guest is efficiently trapped in its cage is one in which the guest is allowed enough rotational freedom to orientate itself in the channel, and the host molecule is allowed restricted conformational freedom.

These conformational changes involving twisting of the Ni-N(pyridine) bonds is desirable since it is this important feature of Werner complexes that gives them their effective clathrating ability.

CHAPTER 7

CHAPTER 7

GENERAL DISCUSSION AND CONCLUSION

Up till now Werner clathrate systems have been studied using the host complex $Ni(NCS)_2(4\text{-}MePy)_4$ with a variety of guest molecules. An extensive comparative study has been made on all the different clathrates formed with this complex, investigating molecular structure and packing, trends in conformation and separation abilities, as well as host-host and host-guest interactions.

In this study, two new Werner clathrate structures have been successfully solved. Investigations through various techniques have illustrated the driving force for clathration, analogous to that found in the study of clathrates formed by $Ni(NCS)_2(4\text{-}MePy)_4$. Thus the ability of a complex to undergo a change from the non-clathrating α- to the clathrating β-modification depends critically on the shape of the potential guest molecules as well as that of the host ligands.

Inconsistent with the results found by Allison and Barrer[23], discussed in Chapter 1, we discovered that the host complex having 3-methylpyridine as ligand was in fact able to form a clathrating b-structure. The guest was the solvent molecule, chloroform, and not the intended aromatic molecule, p-Xylene. Even though chloroform is a stronqly polar molecule, it was able to fit into the cavities formed by the host structure, or more correctly, the host molecule was able to adapt its molecular conformation about the 3-methylpyridine and isothiocyanate ligands to form a cavity to accommodate the $CHCl_3$ molecule. When this happened, the energy environment of the structure was a favourable one, i.e. the host-guest interactions were large enough to trap the guest inside in selected positions.

Thus, contrary to the propositions made in Chapter 1 about the types of guests and hosts, we have proved that the 3-methylpyridine ligand on the host does <u>not</u> retard clathrate formation, and that guest molecules other than aromatics are definitely clathrated.

In our chloroform clathrate, we had initially attempted to enclose p-

Xylene into the host lattice whose ligands contained bulky methyl groups in the meta-positions of each pyridine ring. It would appear that even though the host molecule was able to form cages and channels, the pyridine ligands were unable to twist themselves effectively enough to accommodate the shape of the p-Xylene molecule. Thus large repulsive forces between p-Xylene and 3-methylpyridine would have resulted in an energetically unfavourable conformation. Furthermore, chloroform was in excess to p-Xylene and could compete for site occupancy in the lattice.

It seems too, that size of guest plays a dominant role in clathration. Despite its polarity, chloroform has smaller dimensions than p-Xylene, and was able to adapt its configuration about the two-fold axis to satisfy symmetry requirements of the space group, only by invoking disorder. It was able to fit quite tightly and snugly in the crystalline lattice to give maximum cohesion with the aid of van der Waals forces[4, 77]. Potential energy investigations (Chapter 6) proved that the residual attractions between host-host and host-guest brought about efficient packing.

In a recent study, Kitamura and Nakai[78] have succeeded in forming an octahedral β-type clathrate of $Ni(NCS)_2$ $(4\text{-}MePy)_4$with chloroform in a ratio of 1:0.54 of host:guest. X-ray diffraction patterns were obtained for these crystals, but unfortunately their molecular structure was not elucidated. A more detailed study of this clathrate would have served well for comparative purposes with the analogous structure solved in this study, i.e. $Ni(NCS)_2(3\text{-}MePy)_4.CHCl_3$.

The host molecule of the structure discussed in Chapter 3, namely $Ni(NCS)_2(4\text{-}PhPy)_4.4DMSO$, formed large cavities by virtue of the extended 4-phenylpyridine ligands. Thus, in excess DMSO, the intended guest (m-Xylene) had to compete for occupancy in the host lattice.

By placing the m-Xylene in the centre of this very large void, the distance from this guest to the surrounding host molecules is more than the sum of the van der Waals distances. Since these are important forces decisive for clathration, contraction of the host lattice would not have been enough to effect stabilization by the inclusion of

such a small molecule. In general, a small molecule is able to pass through the host lattice without meeting the inward repulsion which is necessary to stabilize the compound[4]. It seems, therefore, that the total size of four solvent molecules (i.e. DMSO) was more favoured than the size of one or more m-Xylene molecules. The molar ratio 1:4 of host:guest has not yet been observed in any recent studies on Werner clathrates.

The potential energy maps of this structure, discussed in Chapter 6, showed that the two channels exhibited different patterns. The positions of the energy minima found in Channel I differ from those found in Channel II, and are furthermore not symmetrically related to each other. It was also observed that in general the potential energy of Channel II was lower than that of Channel I, due to the different molecular conformation of host molecules surrounding the channels.

Chapter 5 dealt with the stability of the β-phase modification of the chloroform clathrate. An analogous experiment was not performed on the DMSO clathrate crystals due to the extreme difficulty in reproducing the crystals in the same stoicheiometric ratios.

Experimentation undertaken by Allison and Barrer[23] on the β-phase structure of the $Ni(NCS)_2(4\text{-}MePy)_4$ complex established that it was relatively stable in the complete absence of guest species. It produced an open structure allowing the guest to leave and enter freely.

Kemula, Lipkowski and Sybilska[66] also mentioned that the structures which they investigated, where the ligand was 4-methylpyridine, have shown a relatively open structure, in contrast to some typical clathrates where, for guest desorption, host structures have to be destroyed.

Our results were consistent with these observations, though our ligand was 3-methylpyridine. The complex $Ni(NCS)_2(3\text{-}MePy)_4$ showed β-phase structure retention when the guest was desorbed from the lattice. The X-ray powder photographs after guest desorption were identical to those taken before guest desorption.

It was interesting to see that the reflections of the 1:2 clathrate gave X-ray powder lines with identical interplanar spacings to the 1:1 clathrate. Thus we can make the assumption that the crystalline framework of the two clathrates is the same.

Conclusion

This work outlined the general development of clathrate chemistry in the past, and some recent trends.

Knowledge concerning clathrates formed by 4-methylpyridine ligand complexes is being extended to those formed by other ligands, such as 3-methylpyridine and 4-phenylpyridine, to understand in a qualitative sense the properties of the clathrates and the clathration process. In a previous study it was shown that host complexes other than the traditional MX_2A_4 type were also able to form clathrates. For example, a complex of the type $MX_2A_2B_2$ (where M = Ni, X = NCS, A = 4-methylpyridine and B = 4-phenylpyridine) formed a clathrate with methylcellosolve[79].

Knowledge of the structures is necessary in order to interpret the data, not only for selective clathration of guest molecules, but also for host-guest interactions in the clathrate adducts[32].

Since selectivities are hard to foresee, clathrate chemistry has become an extensive study which should progress in such a way as to permit the prediction of specific compounds which will be selectively clathrated by any given host complex[21]. This involves more research, both theoretical and experimental, to elucidate effectively the optimization of the clathration mechanism. With recent developments in crystal packing theory, and the availability of powerful computer programs, structures are solved efficiently and potential energy minima may be calculated, enabling the prediction of complete void design in the foreseeable future.

APPENDIX I

THE OBSERVED AND CALCULATED STRUCTURE FACTORS FOR "METAXY"

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
4	0	0	105	111	-11	1	0	13	-7	-17	2	0	34	35	18	2	0	25	-22	5	3	0	55	56
6	0	0	176	-176	-9	1	0	9	20	-16	2	0	12	-13	21	2	0	7	5	6	3	0	7	-2
7	0	0	50	-46	-7	1	0	22	-21	-15	2	0	44	-43	23	2	0	33	32	8	3	0	29	28
8	0	0	62	56	-6	1	0	104	94	-14	2	0	23	19	24	2	0	7	1	9	3	0	35	-37
9	0	0	30	27	-5	1	0	84	-89	-13	2	0	68	64	25	2	0	16	-20	10	3	0	8	-14
10	0	0	27	-33	-4	1	0	41	33	-11	2	0	12	-21	26	2	0	11	-8	11	3	0	14	-9
11	0	0	18	-18	-3	1	0	63	-58	-10	2	0	32	-33	-26	3	0	7	7	12	3	0	6	6
12	0	0	8	12	4	1	0	30	26	-9	2	0	41	37	-24	3	0	22	-22	13	3	0	50	-44
13	0	0	40	41	5	1	0	97	88	-8	2	0	40	-36	-23	3	0	7	7	14	3	0	13	-14
14	0	0	28	-24	6	1	0	111	110	-7	2	0	76	-68	-22	3	0	10	14	15	3	0	15	14
15	0	0	13	-11	7	1	0	71	68	-6	2	0	25	-19	-21	3	0	20	-14	16	3	0	22	-22
16	0	0	68	65	8	1	0	32	33	-5	2	0	13	4	-19	3	0	17	-14	17	3	0	7	-10
17	0	0	16	17	9	1	0	66	-62	-4	2	0	47	48	-17	3	0	7	-7	18	3	0	12	12
18	0	0	19	-22	10	1	0	31	-19	-3	2	0	180	181	-16	3	0	42	-40	19	3	0	15	13
19	0	0	26	-22	11	1	0	29	24	-2	2	0	58	53	-15	3	0	11	15	21	3	0	12	12
20	0	0	18	-18	13	1	0	42	-45	-1	2	0	188	184	-14	3	0	25	27	23	3	0	11	8
21	0	0	15	-12	14	1	0	39	-43	0	2	0	59	54	-13	3	0	15	17	24	3	0	25	-25
22	0	0	16	-16	15	1	0	37	38	1	2	0	156	-160	-12	3	0	15	-10	25	3	0	10	-10
23	0	0	14	-14	16	1	0	41	42	2	2	0	85	83	-11	3	0	12	16	-25	4	0	20	-20
24	0	0	26	28	17	1	0	14	-12	3	2	0	161	-167	-10	3	0	16	-17	-23	4	0	33	29
25	0	0	12	12	18	1	0	25	-28	4	2	0	55	55	-9	3	0	6	9	-22	4	0	8	2
26	0	0	11	-11	20	1	0	11	11	5	2	0	15	14	-8	3	0	10	-19	-21	4	0	14	-14
-25	1	0	20	20	21	1	0	22	22	6	2	0	43	-45	-7	3	0	32	31	-20	4	0	8	6
-24	1	0	7	9	22	1	0	12	-14	7	2	0	24	24	-6	3	0	26	20	-19	4	0	17	15
-23	1	0	31	-31	23	1	0	8	7	8	2	0	71	-71	-5	3	0	55	-57	-17	4	0	14	-14
-22	1	0	8	2	24	1	0	36	35	9	2	0	17	-19	-4	3	0	39	31	-16	4	0	13	-10
-21	1	0	12	-9	25	1	0	11	-6	10	2	0	26	-22	-3	3	0	80	-84	-15	4	0	40	37
-19	1	0	13	-10	26	1	0	26	-21	11	2	0	20	20	-2	3	0	87	85	-14	4	0	23	19
-17	1	0	34	33	-26	2	0	7	8	12	2	0	30	34	-1	3	0	29	26	-13	4	0	41	-40
-16	1	0	12	-10	-24	2	0	29	-25	13	2	0	28	-25	0	3	0	115	-103	-12	4	0	23	-23
-15	1	0	52	-53	-23	2	0	23	-19	14	2	0	11	-9	1	3	0	13	10	-10	4	0	10	-7
-14	1	0	15	-15	-22	2	0	8	7	15	2	0	43	44	2	3	0	113	105	-9	4	0	19	-18
-13	1	0	25	24	-21	2	0	14	-14	16	2	0	16	-13	3	3	0	85	94	-8	4	0	13	17
-12	1	0	44	-38	-18	2	0	16	15	17	2	0	57	-57	4	3	0	35	27	-7	4	0	51	53
-6	4	0	52	54	-16	5	0	28	29	20	5	0	15	-16	16	6	0	23	23	13	7	0	29	27
-5	4	0	6	1	-15	5	0	42	40	23	5	0	18	-19	17	6	0	11	9	14	7	0	16	-16
-4	4	0	7	-5	-14	5	0	13	-12	25	5	0	12	16	19	6	0	14	-18	16	7	0	22	22
-3	4	0	12	-6	-13	5	0	24	-23	-22	6	0	17	-18	21	6	0	16	18	17	7	0	8	-5
-2	4	0	11	-6	-12	5	0	24	23	-20	6	0	14	14	23	6	0	18	-14	18	7	0	19	-19
-1	4	0	72	-69	-11	5	0	32	29	-16	6	0	14	18	-21	7	0	18	16	19	7	0	10	-7
0	4	0	156	-155	-10	5	0	8	-2	-14	6	0	42	-37	-16	7	0	21	22	20	7	0	13	13
1	4	0	62	59	-9	5	0	10	-8	-13	6	0	13	-11	-14	7	0	22	-26	21	7	0	7	7
2	4	0	17	22	-8	5	0	32	28	-12	6	0	15	19	-13	7	0	6	7	22	7	0	16	-15
3	4	0	35	-40	-7	5	0	50	49	-10	6	0	12	10	-12	7	0	44	42	-17	8	0	8	4
4	4	0	8	-1	-6	5	0	44	-45	-9	6	0	23	23	-11	7	0	11	9	-16	8	0	10	-9
5	4	0	48	-49	-5	5	0	64	-63	-8	6	0	47	43	-10	7	0	32	-30	-15	8	0	12	-6
6	4	0	54	54	-4	5	0	10	-8	-7	6	0	9	3	-9	7	0	13	-9	-14	8	0	9	9
7	4	0	51	-49	-3	5	0	100	95	-6	6	0	9	-11	-8	7	0	17	17	-13	8	0	15	14
8	4	0	8	-1	-2	5	0	51	49	-5	6	0	24	-22	-7	7	0	29	-28	-12	8	0	10	-6
9	4	0	42	43	-1	5	0	124	-119	-4	6	0	12	7	-6	7	0	27	-25	-11	8	0	9	3
10	4	0	17	17	0	5	0	63	59	-3	6	0	23	-15	-5	7	0	10	-2	-10	8	0	14	10
11	4	0	8	6	1	5	0	150	143	-2	6	0	11	-7	-4	7	0	30	33	-9	8	0	9	3
12	4	0	40	-40	2	5	0	17	11	-1	6	0	25	-25	-3	7	0	24	16	-8	8	0	12	-13
13	4	0	18	-20	3	5	0	113	-104	0	6	0	27	34	-2	7	0	12	-9	-7	8	0	13	-17
14	4	0	15	18	4	5	0	27	-28	1	6	0	9	9	-1	7	0	27	27	-6	8	0	10	2
15	4	0	36	-37	5	5	0	45	45	2	6	0	33	-34	0	7	0	26	24	-5	8	0	16	17
16	4	0	38	-36	6	5	0	14	-10	3	6	0	11	-1	1	7	0	43	-43	-4	8	0	15	12
17	4	0	8	10	7	5	0	43	-42	4	6	0	14	14	2	7	0	23	-21	-3	8	0	43	-39
18	4	0	9	11	8	5	0	7	7	5	6	0	30	27	3	7	0	15	-7	-2	8	0	15	-7
19	4	0	12	13	9	5	0	11	9	6	6	0	17	18	4	7	0	29	29	-1	8	0	36	33
22	4	0	12	12	10	5	0	7	0	7	6	0	13	-8	5	7	0	12	7	0	8	0	13	4
24	4	0	19	-17	11	5	0	60	-62	8	6	0	64	61	6	7	0	28	-28	1	8	0	48	-46
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9	-7	9	16	19	10	-5	9	14	-14	-6	-3	9	9	7	-6	-1	9	8	-9	-5	1	9	9	10
11	-7	9	8	-7	11	-5	9	7	12	-4	-3	9	11	9	-2	-1	9	9	-10	-3	1	9	13	-12
15	-7	9	12	-15	15	-5	9	11	10	-2	-3	9	11	16	-1	-1	9	12	-8	-1	1	9	8	6
16	-7	9	10	7	16	-5	9	17	19	-1	-3	9	9	-8	1	-1	9	16	15	0	1	9	10	5
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-9	-6	9	12	13	18	-5	9	14	-15	2	-3	9	18	22	4	-1	9	8	5	2	1	9	14	-17
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-5	-6	9	11	-6	-12	-4	9	14	-14	16	-3	9	27	-26	11	-1	9	18	-13	5	1	9	10	-12
-3	-6	9	12	-14	-10	-4	9	18	16	17	-3	9	16	-17	15	-1	9	13	-12	8	1	9	8	9
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2	-6	9	16	-16	-5	-4	9	9	-6	-9	-2	9	19	-15	-10	0	9	17	-17	11	1	9	11	14
8	-6	9	9	8	-2	-4	9	22	17	-8	-2	9	7	-6	-9	0	9	7	3	12	1	9	13	12
9	-6	9	8	11	0	-4	9	16	-16	-7	-2	9	9	11	-8	0	9	16	16	14	1	9	9	-13
10	-6	9	18	-16	1	-4	9	20	-22	-2	-2	9	9	7	-6	0	9	15	-19	-6	2	9	9	5
16	-6	9	27	22	2	-4	9	20	19	-1	-2	9	10	-13	-5	0	9	8	5	-5	2	9	13	14
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-10	-5	9	11	10	9	-4	9	30	-24	4	-2	9	12	-10	3	0	9	17	-12	2	2	9	8	-2
-9	-5	9	31	32	10	-4	9	17	17	9	-2	9	18	19	4	0	9	13	15	3	2	9	12	12
-8	-5	9	7	-3	11	-4	9	21	22	10	-2	9	16	12	8	0	9	11	9	4	2	9	10	5
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-3	-5	9	14	-15	14	-4	9	14	13	16	-2	9	24	-22	10	0	9	16	-20	8	2	9	8	3
-1	-5	9	21	19	15	-4	9	22	21	17	-2	9	10	12	11	0	9	8	-7	9	2	9	9	-11
0	-5	9	16	17	16	-4	9	17	-19	18	-2	9	7	10	12	0	9	9	11	11	2	9	12	14
1	-5	9	27	-24	17	-4	9	31	-30	-12	-1	9	10	11	15	0	9	13	-10	-2	3	9	8	4
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3	-5	9	14	16	-14	-3	9	8	10	-10	-1	9	10	-13	-9	1	9	10	9	0	3	9	8	-9
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8	-5	9	12	12	-9	-3	9	10	-10	-8	-1	9	10	9	-7	1	9	8	-6	2	3	9	12	10
3	3	9	11	9	-1	-6	10	18	18	-5	-4	10	9	-9	5	-2	10	9	11	9	0	10	14	-14
4	3	9	13	-10	5	-6	10	16	-14	-3	-4	10	7	-9	6	-2	10	16	-16	10	0	10	8	7
5	3	9	10	-8	7	-6	10	19	20	-1	-4	10	13	-17	7	-2	10	7	-6	0	1	10	10	-13
-1	-10	10	15	-12	9	-6	10	10	-8	1	-4	10	8	3	8	-2	10	18	16	2	1	10	8	8
3	-10	10	7	-10	-10	-5	10	12	13	2	-4	10	9	-10	-7	-1	10	11	-10	1	-7	11	10	12
5	-10	10	12	11	-9	-5	10	10	-13	5	-4	10	12	15	-6	-1	10	8	-6	2	-7	11	7	8
6	-9	10	14	-14	-8	-5	10	19	-18	7	-4	10	20	-18	-3	-1	10	7	-5	4	-7	11	10	-10
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6	-8	10	16	-15	-2	-5	10	10	10	15	-4	10	9	-11	7	-1	10	14	15	5	-6	11	14	16
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-9	-7	10	8	9	0	-5	10	27	-25	-7	-3	10	9	10	9	-1	10	11	-10	-3	-5	11	13	9
-7	-7	10	13	-13	3	-5	10	12	-13	-3	-3	10	8	-5	-4	0	10	9	-7	2	-5	11	8	-6
-2	-7	10	8	-8	4	-5	10	17	-17	-2	-3	10	9	-5	-3	0	10	10	-6	5	-5	11	15	15
4	-7	10	15	-13	5	-5	10	9	7	-1	-3	10	19	-21	-2	0	10	12	16	6	-5	11	19	-17
5	-7	10	17	-14	6	-5	10	33	30	0	-3	10	7	9	-1	0	10	19	19	7	-5	11	16	-16
7	-7	10	14	14	8	-5	10	22	-26	4	-3	10	8	4	0	0	10	11	-11	8	-5	11	16	16
11	-7	10	10	9	10	-5	10	15	15	5	-3	10	16	14	1	0	10	13	-13	4	-4	11	11	10
-8	-6	10	11	-7	12	-5	10	15	-15	7	-3	10	16	-16	2	0	10	8	9	6	-4	11	15	-15
-7	-6	10	10	-8	14	-5	10	11	12	9	-3	10	10	10	5	0	10	14	-13	1	-3	11	7	-6
-3	-6	10	12	-12	-9	-4	10	11	-11	-8	-2	10	15	14	7	0	10	22	21	5	-3	11	11	-13
-2	-6	10	8	-10	-7	-4	10	12	13	0	-2	10	14	16	8	0	10	7	-7	6	-3	11	11	-11

APPENDIX II

THE OBSERVED AND CALCULATED STRUCTURE FACTORS FOR "PARA" - MODEL A

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
4	0	0	1036	-903	0	12	0	308	-230	15	5	1	113	-105	15	13	1	164	-149	3	21	1	97	93
8	0	0	177	140	12	12	0	52	57	19	5	1	46	48	17	13	1	60	66	5	21	1	44	-19
12	0	0	507	-516	16	12	0	150	-145	1	7	1	280	-225	19	13	1	88	92	9	21	1	80	80
16	0	0	251	228	6	14	0	106	75	5	7	1	58	-13	21	13	1	79	-87	13	21	1	57	-40
20	0	0	58	-33	0	16	0	63	32	7	7	1	45	-87	25	13	1	88	90	15	21	1	46	-45
24	0	0	221	223	4	16	0	70	63	11	7	1	122	86	1	15	1	289	-246	9	23	1	58	-59
28	0	0	172	-175	12	16	0	61	49	13	7	1	129	137	3	15	1	253	265	9	25	1	52	-42
6	2	0	960	-780	20	16	0	67	64	15	7	1	119	-133	5	15	1	145	169	6	0	2	642	650
10	2	0	429	452	2	18	0	129	-140	19	7	1	50	58	7	15	1	112	-116	10	0	2	411	-331
18	2	0	242	205	10	18	0	87	-51	1	9	1	97	-119	9	15	1	314	-300	14	0	2	86	96
22	2	0	219	-214	14	18	0	85	93	3	9	1	158	-156	11	15	1	142	120	18	0	2	207	-191
26	2	0	86	94	0	20	0	122	105	5	9	1	185	-116	13	15	1	175	185	22	0	2	217	198
0	4	0	496	-426	4	20	0	173	-157	7	9	1	117	112	15	15	1	182	-187	26	0	2	98	-107
4	4	0	776	-828	8	20	0	100	89	9	9	1	51	51	17	15	1	67	-61	4	2	2	725	-715
8	4	0	112	50	12	20	0	49	-57	15	9	1	89	65	19	15	1	89	101	6	2	2	68	-42
12	4	0	650	579	2	22	0	67	68	21	9	1	67	48	21	15	1	51	53	8	2	2	279	260
16	4	0	440	-427	14	22	0	86	-77	25	9	1	58	-56	1	17	1	155	-155	12	2	2	470	-396
24	4	0	59	-54	0	24	0	94	80	1	11	1	172	148	3	17	1	215	-225	16	2	2	432	415
28	4	0	82	71	12	24	0	95	92	3	11	1	240	-275	5	17	1	79	74	24	2	2	130	107
2	6	0	260	191	2	26	0	46	-45	5	11	1	64	57	7	17	1	139	112	28	2	2	113	-115
6	6	0	379	371	5	1	1	358	288	7	11	1	53	2	9	17	1	204	-207	2	4	2	371	296
10	6	0	401	-354	7	1	1	100	96	9	11	1	175	203	11	17	1	77	-79	4	4	2	404	-368
14	6	0	81	81	3	3	1	122	180	11	11	1	62	-35	13	17	1	139	119	6	4	2	425	-430
18	6	0	171	-169	5	3	1	66	-23	13	11	1	86	-120	15	17	1	121	117	8	4	2	205	207
22	6	0	124	127	7	3	1	132	176	15	11	1	103	129	17	17	1	55	-40	10	4	2	477	490
26	6	0	46	-29	11	3	1	67	-60	21	11	1	47	-26	19	17	1	69	-72	14	4	2	120	-112
0	8	0	535	422	13	3	1	169	-186	25	11	1	85	61	21	17	1	64	49	18	4	2	169	168
4	8	0	113	-64	15	3	1	81	85	1	13	1	258	280	1	19	1	185	167	22	4	2	165	-156
8	8	0	143	-35	1	5	1	255	-257	3	13	1	298	298	3	19	1	214	-210	26	4	2	65	44
12	8	0	111	-92	3	5	1	45	19	5	13	1	203	-166	7	19	1	116	111	0	6	2	736	-684
16	8	0	185	183	5	5	1	89	-136	7	13	1	216	-212	9	19	1	83	72	2	6	2	43	-52
20	8	0	96	95	9	5	1	362	313	9	13	1	235	241	13	19	1	56	-50	4	6	2	252	-194
10	10	0	136	159	11	5	1	85	78	11	13	1	107	119	15	19	1	83	73	6	6	2	243	-242
22	10	0	70	-57	13	5	1	209	-186	13	13	1	174	-162	1	21	1	105	90	10	6	2	106	108
12	6	2	268	268	8	18	2	96	-88	9	5	3	174	137	3	13	3	83	-87	11	21	3	52	-14
14	6	2	67	105	12	18	2	75	79	11	5	3	101	-96	9	13	3	121	158	13	21	3	53	-49
16	6	2	224	-221	20	18	2	45	36	15	5	3	177	173	13	13	3	208	-192	15	21	3	67	62
18	6	2	60	-74	2	20	2	99	-107	17	5	3	51	45	15	13	3	162	160	1	23	3	57	54
24	6	2	51	-56	4	20	2	51	44	21	5	3	49	-50	19	13	3	70	-82	3	23	3	81	75
28	6	2	70	60	8	20	2	48	-59	25	5	3	72	73	1	15	3	130	124	7	23	3	48	-45
4	8	2	56	-89	14	20	2	62	70	1	7	3	89	-55	3	15	3	185	186	0	0	4	277	-101
6	8	2	212	194	12	22	2	77	-67	3	7	3	105	117	7	15	3	161	-177	4	0	4	792	-737
10	8	2	118	-166	2	24	2	62	65	5	7	3	127	-45	9	15	3	179	156	8	0	4	98	-99
14	8	2	70	-65	4	24	2	56	46	9	7	3	226	305	11	15	3	127	122	12	0	4	598	580
16	8	2	54	-48	6	24	2	45	-41	15	7	3	45	-61	13	15	3	123	-130	16	0	4	406	-397
18	8	2	82	-77	10	24	2	58	52	17	7	3	55	-49	15	15	3	84	-90	28	0	4	72	55
22	8	2	107	99	0	26	2	56	-47	19	7	3	78	87	17	15	3	54	61	2	2	4	184	-157
0	10	2	526	565	4	26	2	56	51	23	7	3	45	-38	19	15	3	60	77	4	2	4	441	-372
2	10	2	89	77	1	1	3	118	27	1	9	3	402	-393	21	15	3	65	-68	6	2	4	288	286
4	10	2	71	41	3	1	3	161	163	3	9	3	272	279	1	17	3	190	-196	8	2	4	363	348
10	10	2	58	-70	5	1	3	92	-123	9	9	3	296	-249	3	17	3	246	223	10	2	4	510	-492
12	10	2	138	-155	7	1	3	94	96	11	9	3	51	77	7	17	3	163	-156	12	2	4	75	-109
16	10	2	139	150	13	1	3	129	91	13	9	3	228	216	9	17	3	81	-118	14	2	4	212	156
20	10	2	51	56	15	1	3	81	-72	15	9	3	188	-191	11	17	3	113	114	16	2	4	54	-50
22	10	2	62	47	17	1	3	59	-49	25	9	3	57	-75	13	17	3	139	141	18	2	4	150	-155
6	12	2	196	-208	27	1	3	57	58	1	11	3	205	-153	15	17	3	136	-136	20	2	4	56	63
10	12	2	152	111	1	3	3	386	-351	3	11	3	411	-404	17	17	3	76	-85	22	2	4	132	142
12	12	2	53	31	3	3	3	328	-273	5	11	3	65	83	21	17	3	46	56	26	2	4	51	-55
14	12	2	94	57	5	3	3	152	-203	7	11	3	276	265	1	19	3	97	-85	0	4	4	1710	1423
18	12	2	54	37	9	3	3	264	-241	9	11	3	207	-206	3	19	3	72	-64	2	4	4	179	109
0	14	2	155	-194	11	3	3	73	-61	11	11	3	125	-131	5	19	3	114	93	4	4	4	492	-412
6	14	2	72	66	19	3	3	74	-76	13	11	3	82	78	9	19	3	154	-159	6	4	4	137	-155
8	14	2	48	34	21	3	3	123	125	15	11	3	87	101	13	19	3	69	84	8	4	4	139	212
16	14	2	71	-73	23	3	3	57	57	17	11	3	62	-61	15	19	3	70	69	12	4	4	222	-233
2	16	2	84	86	1	5	3	279	259	19	11	3	78	-71	19	19	3	69	-69	14	4	4	50	-32
14	16	2	107	-90	3	5	3	613	-612	21	11	3	101	111	1	21	3	56	67	16	4	4	220	223
4	18	2	110	111	5	5	3	332	308	25	11	3	69	-86	3	21	3	63	-68	24	4	4	105	88
6	18	2	55	-54	7	5	3	45	-89	1	13	3	269	287	9	21	3	53	71	28	4	4	95	-87

M	K	L	FO	FC	M	K	L	FO	FC	M	K	L	FO	FC	M	K	L	FO	FC	M	K	L	FO	FC
2	6	4	261	231	6	14	4	75	-56	3	3	5	65	-36	19	9	5	119	121	9	17	5	141	142
4	6	4	456	-500	16	14	4	46	49	5	3	5	75	70	21	9	5	59	-74	13	17	5	58	-45
6	6	4	283	-366	24	14	4	47	-34	7	3	5	136	117	23	9	5	84	-79	19	17	5	70	71
8	6	4	50	72	0	16	4	74	-54	9	3	5	152	108	25	9	5	59	59	1	19	5	126	-124
10	6	4	234	222	2	16	4	83	-62	13	3	5	127	108	1	11	5	413	-385	3	19	5	57	90
12	6	4	102	-79	4	16	4	70	-54	15	3	5	178	-175	3	11	5	216	224	9	19	5	93	-108
18	6	4	100	88	6	16	4	44	48	21	3	5	81	-86	5	11	5	211	163	13	19	5	94	109
22	6	4	100	-92	8	16	4	51	50	27	3	5	60	59	9	11	5	160	-157	15	19	5	80	-88
26	6	4	59	53	14	16	4	46	47	3	5	5	229	-230	13	11	5	128	155	1	21	5	52	-50
0	8	4	625	-599	18	16	4	48	-36	5	5	5	264	325	15	11	5	184	-199	3	21	5	84	-96
2	8	4	211	186	2	18	4	84	85	7	5	5	334	331	19	11	5	61	65	7	21	5	97	98
4	8	4	97	24	8	18	4	82	85	9	5	5	81	-61	23	11	5	47	-31	9	21	5	73	-81
6	8	4	51	-74	12	18	4	62	-51	19	5	5	106	-116	25	11	5	50	-56	11	21	5	57	-64
10	8	4	102	105	14	18	4	63	-72	21	5	5	124	121	3	13	5	201	-191	13	21	5	52	60
12	8	4	179	163	10	20	4	51	-34	23	5	5	46	65	7	13	5	212	214	1	23	5	99	90
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15	13	13	94	91	16	2	14	85	-97	8	14	14	46	42	5	13	15	47	58	2	4	16	64	-42
17	13	13	70	-66	20	2	14	99	111	14	14	14	50	-34	7	13	15	90	-93	4	4	16	156	156
1	15	13	92	98	2	4	14	210	-207	4	16	14	50	-40	9	13	15	69	-51	6	4	16	103	97
5	15	13	86	-79	4	4	14	42	28	0	18	14	84	85	11	13	15	103	89	8	4	16	188	-190
10	4	16	50	-47	1	9	17	47	-42	14	0	18	95	80	11	7	19	75	73	4	6	20	55	-33
12	4	16	101	112	5	9	17	95	79	0	2	18	91	95	13	7	19	80	-66	6	6	20	79	-78
16	4	16	53	-74	9	9	17	57	-60	4	2	18	137	-139	1	9	19	80	-72	10	6	20	69	63
20	4	16	66	80	11	9	17	76	-65	6	2	18	62	-52	5	9	19	80	70	0	8	20	47	-51
2	6	16	90	-92	13	9	17	78	62	8	2	18	111	123	7	9	19	73	-66	4	8	20	85	84
6	6	16	46	-32	15	9	17	64	45	12	2	18	53	-58	9	9	19	59	-48	8	8	20	72	-78
8	6	16	55	36	1	11	17	83	90	2	4	18	80	96	13	9	19	52	39	12	8	20	53	58
14	6	16	112	107	5	11	17	91	-83	10	4	18	64	86	1	11	19	53	-51	4	12	20	48	-26
0	8	16	44	16	7	11	17	50	59	14	4	18	128	-127	3	11	19	57	-60	1	5	21	66	-54
6	8	16	58	32	9	11	17	64	62	18	4	18	56	46	11	11	19	76	-81	3	5	21	49	-61
8	8	16	58	64	11	11	17	68	-56	2	6	18	52	40	1	13	19	85	77	1	7	21	67	70
10	8	16	56	-52	15	11	17	52	49	4	6	18	75	95	5	13	19	76	-87	5	7	21	59	-61
2	10	16	107	95	1	13	17	94	98	8	6	18	100	-102	7	13	19	67	50	7	7	21	64	69
14	10	16	64	-70	3	13	17	79	90	12	6	18	70	67	9	13	19	74	55	1	9	21	72	66
8	12	16	70	-73	5	13	17	46	-53	2	8	18	108	-108	1	15	19	60	63	3	9	21	69	73
12	12	16	45	32	7	13	17	63	-57	6	8	18	56	41	5	15	19	63	-44	7	9	21	52	-45
3	1	17	59	-67	11	13	17	85	83	10	8	18	71	-59	4	0	20	50	60	3	11	21	46	31
13	1	17	44	18	13	13	17	51	-48	14	8	18	85	80	8	0	20	64	-68	5	11	21	59	57
15	1	17	47	-24	1	15	17	111	-100	6	10	18	50	-28	12	0	20	69	73	4	2	22	45	49
1	3	17	84	80	3	15	17	53	64	8	10	18	54	66	2	2	20	57	-76	2	4	22	138	-131
3	5	17	69	79	5	15	17	73	60	7	5	19	68	71	14	2	20	67	78	6	4	22	62	69
11	5	17	72	83	7	15	17	90	-89	9	5	19	48	32	0	4	20	64	68	0	6	22	95	82
13	5	17	47	-48	11	15	17	58	59	11	5	19	57	-54	4	4	20	84	-91	4	6	22	74	-85
1	7	17	52	-43	1	17	17	94	-88	1	7	19	86	83	6	4	20	52	38	8	6	22	64	54
7	7	17	64	-70	5	17	17	81	83	3	7	19	69	67	8	4	20	62	76	2	8	22	52	66
15	7	17	48	-31	2	0	18	267	-279	5	7	19	86	-68	12	4	20	51	-53	1	5	23	57	-48
17	7	17	55	-61	6	0	18	94	84	9	7	19	46	45	2	6	20	149	141					

APPENDIX III

THE OBSERVED AND CALCULATED STRUCTURE FACTORS FOR "PARA" - MODEL B

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
4	0	0	1037	-1040	0	12	0	308	-291	15	5	1	114	-97	15	13	1	164	-152	3	21	1	97	94
8	0	0	177	106	12	12	0	52	53	19	5	1	46	45	17	13	1	60	61	5	21	1	44	-22
12	0	0	508	-455	16	12	0	150	-147	1	7	1	280	-242	19	13	1	88	93	9	21	1	80	82
16	0	0	251	236	6	14	0	106	89	5	7	1	58	83	21	13	1	79	-86	13	21	1	57	-43
20	0	0	58	-53	0	16	0	63	60	7	7	1	45	-55	25	13	1	88	89	15	21	1	46	-49
24	0	0	221	236	4	16	0	70	58	11	7	1	122	88	1	15	1	289	-274	9	23	1	58	-62
28	0	0	172	-167	12	16	0	61	55	13	7	1	129	123	3	15	1	253	259	9	25	1	52	-42
6	2	0	961	-754	20	16	0	67	62	15	7	1	119	-141	5	15	1	145	170	6	0	2	643	683
10	2	0	430	413	2	18	0	129	-143	19	7	1	50	50	7	15	1	112	-104	10	0	2	412	-387
18	2	0	242	222	10	18	0	87	-51	1	9	1	97	-101	9	15	1	315	-295	14	0	2	86	58
22	2	0	219	-206	14	18	0	85	78	3	9	1	158	-163	11	15	1	142	135	18	0	2	207	-179
26	2	0	86	96	0	20	0	122	101	5	9	1	186	-200	13	15	1	175	188	22	0	2	218	213
0	4	0	496	-397	4	20	0	174	-158	7	9	1	117	123	15	15	1	182	-185	26	0	2	98	-104
4	4	0	777	-703	8	20	0	100	84	9	9	1	51	-21	17	15	1	67	-62	4	2	2	726	-599
8	4	0	112	97	12	20	0	49	-56	15	9	1	89	59	19	15	1	89	103	6	2	2	68	-44
12	4	0	651	541	2	22	0	67	66	21	9	1	67	51	21	15	1	51	54	8	2	2	279	314
16	4	0	441	-435	14	22	0	86	-78	25	9	1	58	-57	1	17	1	155	-140	12	2	2	471	-443
24	4	0	60	-59	0	24	0	94	80	1	11	1	172	175	3	17	1	215	-225	16	2	2	433	409
28	4	0	82	65	12	24	0	95	93	3	11	1	240	-282	5	17	1	79	75	24	2	2	131	117
2	6	0	261	173	2	26	0	46	-44	5	11	1	64	33	7	17	1	139	121	28	2	2	114	-109
6	6	0	379	278	5	1	1	358	202	7	11	1	53	-30	9	17	1	204	-212	2	4	2	371	285
10	6	0	401	-406	7	1	1	100	86	9	11	1	175	150	11	17	1	77	-71	4	4	2	405	-467
14	6	0	81	97	3	3	1	122	136	11	11	1	62	-38	13	17	1	139	122	6	4	2	426	-503
18	6	0	171	-166	5	3	1	66	-75	13	11	1	87	-111	15	17	1	121	122	8	4	2	206	183
22	6	0	124	123	7	3	1	132	147	15	11	1	104	128	17	17	1	55	-45	10	4	2	478	472
26	6	0	46	-28	11	3	1	67	-41	21	11	1	47	-30	19	17	1	69	-74	14	4	2	120	-93
0	8	0	536	490	13	3	1	169	-150	25	11	1	85	65	21	17	1	64	53	18	4	2	170	160
4	8	0	113	-130	15	3	1	82	75	1	13	1	258	242	1	19	1	185	171	22	4	2	165	-165
8	8	0	143	-113	1	5	1	255	-239	3	13	1	298	308	3	19	1	214	-207	26	4	2	66	49
12	8	0	111	-90	3	5	1	45	27	5	13	1	203	-147	7	19	1	116	108	0	6	2	737	-639
16	8	0	185	192	5	5	1	89	17	7	13	1	216	-229	9	19	1	83	74	2	6	2	44	-49
20	8	0	96	95	9	5	1	362	364	9	13	1	235	265	13	19	1	56	-48	4	6	2	252	-279
10	10	0	137	192	11	5	1	85	93	11	13	1	107	105	15	19	1	83	74	6	6	2	244	-213
22	10	0	70	-58	13	5	1	209	-222	13	13	1	174	-158	1	21	1	105	90	10	6	2	106	103
12	6	2	268	282	8	18	2	96	-75	9	5	3	175	179	3	13	3	83	-85	11	21	3	52	-14
14	6	2	67	97	12	18	2	75	89	11	5	3	101	-101	9	13	3	121	173	13	21	3	53	-49
16	6	2	224	-207	20	18	2	45	33	15	5	3	177	179	13	13	3	208	-195	15	21	3	67	60
18	6	2	60	-76	2	20	2	99	-105	17	5	3	51	48	15	13	3	162	165	1	23	3	57	56
24	6	2	51	-67	4	20	2	51	46	21	5	3	49	-54	19	13	3	71	-82	3	23	3	82	74
28	6	2	70	55	8	20	2	48	-53	25	5	3	72	78	1	15	3	130	142	7	23	3	48	-46
4	8	2	56	-38	14	20	2	62	68	1	7	3	89	-71	3	15	3	185	179	0	0	4	277	-248
6	8	2	212	279	12	22	2	77	-69	3	7	3	105	82	7	15	3	161	-165	4	0	4	793	-707
10	8	2	118	-111	2	24	2	62	64	5	7	3	127	-165	9	15	3	180	136	8	0	4	98	-55
14	8	2	71	-68	4	24	2	56	45	9	7	3	226	233	11	15	3	127	124	12	0	4	598	574
16	8	2	55	-64	6	24	2	45	-40	15	7	3	45	-62	13	15	3	123	-126	16	0	4	407	-392
18	8	2	82	-85	10	24	2	58	52	17	7	3	55	-31	15	15	3	84	-82	28	0	4	72	51
22	8	2	107	99	0	26	2	56	-49	19	7	3	78	82	17	15	3	54	58	2	2	4	185	-172
0	10	2	526	482	4	26	2	56	51	23	7	3	45	-39	19	15	3	60	75	4	2	4	441	-447
2	10	2	89	91	1	1	3	118	72	1	9	3	402	-361	21	15	3	66	-68	6	2	4	288	239
4	10	2	71	83	3	1	3	161	150	3	9	3	273	242	1	17	3	191	-180	8	2	4	364	340
10	10	2	58	-72	5	1	3	92	-150	9	9	3	296	-293	3	17	3	246	228	10	2	4	510	-486
12	10	2	138	-147	7	1	3	94	85	11	9	3	51	80	7	17	3	163	-170	12	2	4	75	-77
16	10	2	139	138	13	1	3	129	118	13	9	3	229	220	9	17	3	81	-121	14	2	4	212	194
20	10	2	51	50	15	1	3	82	-75	15	9	3	188	-182	11	17	3	113	108	16	2	4	55	-34
22	10	2	62	49	17	1	3	60	-63	25	9	3	57	-73	13	17	3	139	145	18	2	4	150	-155
6	12	2	197	-223	27	1	3	57	57	1	11	3	205	-187	15	17	3	136	-135	20	2	4	56	62
10	12	2	153	107	1	3	3	386	-343	3	11	3	412	-386	17	17	3	77	-87	22	2	4	132	133
12	12	2	53	19	3	3	3	328	-254	5	11	3	66	127	21	17	3	46	56	26	2	4	51	-59
14	12	2	94	65	5	3	3	152	-68	7	11	3	277	258	1	19	3	97	-92	0	4	4	1713	1516
18	12	2	54	38	9	3	3	264	-209	9	11	3	208	-186	3	19	3	72	-67	2	4	4	179	149
0	14	2	155	-147	11	3	3	73	-57	11	11	3	125	-135	5	19	3	114	100	4	4	4	493	-476
6	14	2	72	60	19	3	3	74	-73	13	11	3	82	88	9	19	3	154	-163	6	4	4	137	-130
8	14	2	48	-12	21	3	3	123	130	15	11	3	87	100	13	19	3	69	88	8	4	4	139	153
16	14	2	71	-68	23	3	3	57	59	17	11	3	62	-68	15	19	3	70	72	12	4	4	223	-210
2	16	2	84	73	1	5	3	279	217	19	11	3	78	-73	19	19	3	69	-68	14	4	4	50	-61
14	16	2	107	-91	3	5	3	613	-575	21	11	3	101	108	1	21	3	56	62	16	4	4	220	222
4	18	2	110	105	5	5	3	333	346	25	11	3	69	-83	3	21	3	63	-67	24	4	4	105	95
6	18	2	55	-52	7	5	3	45	-56	1	13	3	269	273	9	21	3	53	72	28	4	4	95	-84

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	6	4	261	251	6	14	4	75	-58	3	3	5	66	-55	19	9	5	120	119	9	17	5	142	144
4	6	4	457	-409	16	14	4	46	49	5	3	5	75	74	21	9	5	59	-77	13	17	5	58	-46
6	6	4	283	-288	24	14	4	47	-32	7	3	5	136	140	23	9	5	84	-82	19	17	5	70	67
8	6	4	50	92	0	16	4	74	-69	9	3	5	153	149	25	9	5	60	65	1	19	5	126	-129
10	6	4	234	259	2	16	4	83	-62	13	3	5	127	126	1	11	5	413	-374	3	19	5	57	83
12	6	4	102	-98	4	16	4	71	-54	15	3	5	178	-170	3	11	5	217	242	9	19	5	93	-108
18	6	4	100	85	6	16	4	44	52	21	3	5	82	-84	5	11	5	211	181	13	19	5	94	104
22	6	4	100	-96	8	16	4	51	55	27	3	5	60	54	9	11	5	160	-152	15	19	5	80	-84
26	6	4	59	55	14	16	4	46	42	3	5	5	229	-261	13	11	5	128	144	1	21	5	52	-52
0	8	4	626	-630	18	16	4	48	-37	5	5	5	264	200	15	11	5	185	-204	3	21	5	84	-94
2	8	4	212	201	2	18	4	84	82	7	5	5	334	320	19	11	5	61	65	7	21	5	98	98
4	8	4	97	75	8	18	4	82	87	9	5	5	81	-108	23	11	5	47	-36	9	21	5	73	-79
6	8	4	51	-70	12	18	4	62	-52	19	5	5	106	-118	25	11	5	50	-57	11	21	5	57	-60
10	8	4	102	105	14	18	4	63	-71	21	5	5	125	123	3	13	5	202	-201	13	21	5	52	61
12	8	4	179	149	10	20	4	51	-37	23	5	5	46	62	7	13	5	213	212	1	23	5	99	92
14	8	4	47	-43	12	20	4	82	84	25	5	5	66	-67	9	13	5	133	-186	3	23	5	71	-66
16	8	4	185	-207	2	22	4	103	-106	1	7	5	447	437	11	13	5	145	-158	2	0	6	126	124
24	8	4	66	-77	4	22	4	64	-70	3	7	5	343	-344	13	13	5	125	133	6	0	6	301	-294
2	10	4	201	-187	6	22	4	79	71	5	7	5	79	-25	15	13	5	80	84	10	0	6	376	365
4	10	4	113	76	10	22	4	55	-37	7	7	5	143	157	17	13	5	77	-59	14	0	6	134	-167
6	10	4	213	191	0	24	4	161	160	11	7	5	144	-137	21	13	5	69	76	18	0	6	150	149
8	10	4	103	97	4	24	4	129	-126	13	7	5	264	-276	1	15	5	116	109	22	0	6	72	-78
10	10	4	109	-144	8	24	4	56	51	15	7	5	160	165	3	15	5	115	-142	0	2	6	418	-332
12	10	4	50	-47	2	26	4	74	82	17	7	5	148	154	5	15	5	74	54	2	2	6	105	106
16	10	4	44	-27	1	1	5	568	-546	25	7	5	84	94	7	15	5	104	76	4	2	6	128	-155
18	10	4	55	-90	3	1	5	77	79	27	7	5	62	-39	9	15	5	101	78	6	2	6	168	148
22	10	4	80	88	5	1	5	375	-285	1	9	5	351	289	11	15	5	98	-86	10	2	6	134	-124
0	12	4	299	271	7	1	5	272	-296	3	9	5	269	267	13	15	5	101	-120	12	2	6	235	219
2	12	4	43	24	9	1	5	95	143	5	9	5	291	-214	15	15	5	125	139	14	2	6	59	-40
6	12	4	62	-69	11	1	5	74	-92	7	9	5	102	-94	17	15	5	58	70	16	2	6	167	-176
12	12	4	62	-80	15	1	5	100	87	9	9	5	310	341	1	17	5	92	80	24	2	6	67	-78
16	12	4	82	90	19	1	5	47	57	11	9	5	123	98	3	17	5	64	76	2	4	6	150	-150
2	14	4	50	-40	21	1	5	50	-42	13	9	5	115	-144	5	17	5	105	-88	4	4	6	417	-357
4	14	4	52	-30	1	3	5	506	-469	15	9	5	83	-71	7	17	5	44	-37	6	4	6	235	221
8	4	6	114	155	8	12	6	85	97	19	1	7	59	50	5	9	7	90	53	13	17	7	52	-50
10	4	6	163	-171	10	12	6	90	-67	21	1	7	75	87	7	9	7	144	181	15	17	7	79	71
12	4	6	109	-105	12	12	6	42	-32	1	3	7	102	-61	9	9	7	120	121	3	19	7	111	107
16	4	6	83	-76	22	12	6	57	56	3	3	7	110	89	11	9	7	144	-199	7	19	7	103	-107
18	4	6	100	-90	0	14	6	42	31	7	3	7	113	-110	13	9	7	245	-273	9	19	7	56	56
20	4	6	45	45	10	14	6	58	-55	9	3	7	178	168	15	9	7	183	201	11	19	7	75	78
22	4	6	96	98	14	14	6	61	-45	11	3	7	109	129	17	9	7	171	183	13	19	7	50	-53
26	4	6	84	-78	18	14	6	45	49	13	3	7	84	82	25	9	7	52	60	17	19	7	57	45
0	6	6	841	666	4	16	6	78	-86	15	3	7	66	70	1	11	7	51	88	1	21	7	93	-93
4	6	6	364	-361	8	16	6	82	-87	19	3	7	48	52	3	11	7	48	47	3	21	7	71	84
6	6	6	48	-85	12	16	6	56	48	21	3	7	45	-40	5	11	7	177	-187	5	21	7	55	41
8	6	6	372	422	10	18	6	75	58	1	5	7	571	-457	7	11	7	165	-131	9	21	7	83	-80
12	6	6	315	-337	12	18	6	51	-26	3	5	7	60	53	9	11	7	222	222	13	21	7	62	68
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