STRUCTURES
OF
WERNER CLATHRATES

A thesis submitted to the
UNIVERSITY OF CAPE TOWN
in fulfilment of the requirements for the degree of
MASTER OF SCIENCE

BY

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March 1982

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ACKNOWLEDGEMENTS

I wish to extend sincere thanks to

Professor L.R. Nassimbeni, for his enthusiastic supervision, patience and good humour,

Dr G.E. Jackson, for his advice and assistance with the N.M.R. work,

all colleagues, for their interest, help and friendship,

my husband William, for his encouragement.

Financial assistance from the A.E. & C.I. is gratefully acknowledged.

This work is dedicated to my Parents.

ABSTRACT

The structures of two new Werner clathrates have been elucidated by X-ray diffraction.

$Ni(NCS)_2(C_6H_7N)_2(C_{11}H_9N)_2$.methyl cellosolve is monoclinic with a = 10,648(5), b = 23,005(12), c = 16,294(8)Å, β = 98,04(2)°, Z = 4 and the space group $C2/c$. The guest, methyl cellosolve is disordered and lies at a centre of inversion.

$Ni(NCS)_2(C_6H_7N)_4$.p-cymene is tetragonal with a = 17,105(9), b = 17,105(9), c = 23,837(12)Å, Z = 8 and the space group $I4_1/a$. The guest, p-cymene is disordered and lies at a centre of inversion.

The stoicheiometry of the clathrates was investigated by various chemical methods including; thermogravimetric analysis, differential thermal analysis, mass spectroscopy and proton nuclear magnetic resonance spectroscopy.

Host-guest non-bonded energy relationships using atom-pair potentials are examined.

Attempts have been made to estimate the association constants of some of these compounds in solution by proton nuclear magnetic resonance spectroscopy.

CONTENTS

CHAPTER 1

CHAPTER 1

INTRODUCTION

More than a century ago new chemical species which did not obey the "normal" rules of combination, were categorised as "Complex Compounds"[1].

Today, the number and variety of these molecular inclusion compounds appear to be without limit. Inclusion compounds are most clearly defined in a negative way, *i.e.* they are compounds which do not form by means of ionic, covalent or coordinate covalent bonds. Furthermore, inclusion is believed to be the result of the ability of one compound to enclose a second spatially. The terms "guest" and "host" have been applied to the enclosed molecule and the enclosing molecular framework respectively. An essential characteristic of the host, is its ability to form a solid structure with void spaces of dimensions large enough to house the prospective guests. The forces operating in the formation of these inclusion compounds are dependent on the type of compound formed.

Inclusion compounds may therefore be sub-classified as the intercalate or layer type, where the guest component is situated between layers of host structure; the channel type, in which the guest species 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.

INTERCALATES OR LAYER TYPE

The simplest compound to have a layered structure is graphite, a carbon allotrope. Due to the large interlayer separation of 3,35Å and the weak van der Waal's interlayer forces, a variety of species such as K, CrO_3, SbF_5 and $AlCl_3$ may penetrate between the layers to form graphite intercalates[2]. These intercalated species have considerable translational mobility within the graphite lattice.

Other systems which do form intercalates are the layered silicates, which have been used to achieve a variety of selective chemical conversions[3], and the transition metal disulphides, of which the Li/TiS_2 intercalate shows promise of being used as a battery system[4,5].

CHANNEL TYPE

Inclusion compounds which have channel-like void space include the well-known urea and thiourea adducts. Urea molecules undergo hydrogen bonding to form open hexagonal channels large enough to accommodate numerous straight-chain hydrocarbon guest molecules[1]. Smith[6,7] suggests that hydrogen bonds of the type, N - H --- O = C account largely for the stability of the complex. In addition, van der Waal's forces between the hydrocarbon guest molecule and the urea host molecules which surround it, contribute to the greater stability of this polynuclear inclusion compound.

The thiourea adducts are similar to those of the urea, but have channels approximately 2Å greater in diameter, hence their ability to accommodate larger, branched-chain guest molecules such as trimethylpentane, cyclo=pentane, cyclohexane and triptane. Urea and thiourea adducts, because of their specificity for unbranched and branched chain molecules respectively, are utilised in an extractive crystallisation method for separation of hydrocarbons[8,9].

The choleic acids are the oldest of the recorded polynuclear inclusion compounds. The more commonly known choleic acid complexes are those of desoxycholic acid. X-ray studies of these inclusion complexes have shown them to have open structures[10] leaving free channels for inclusion of hydrocarbons, esters, alcohols, carboxylic acids, phenols, ethers and alkaloids. Desoxycholic acid molecules are hydrogen bonded to each other and thus produce the series of connected channels.

Inclusion compounds of the choleic acids do not dissociate completely into their components in the liquid phase. This particular characteristic of these complexes provides a method for solubilising fatty acids and insoluble hydrocarbons. The choleic acids have also been used in the separation of components of racemic mixtures[11].

Typical of the monomolecular inclusion compounds are the cyclodextrins, also known as Schardinger dextrins. The cyclodextrins are cycloamyloses consisting of six (α), seven (β) or eight (γ) glucose units in α-1,4-linkage. These torus-shaped molecules have a height of 8Å and the internal channel diameter varies from 5Å in the α-cyclodextrin to 8Å in the γ-cyclodextrin[2]. A wide variety of guest components such as trichloroethylene, toluene, and bromobenzene are trapped within the empty centres of the carbohydrate rings by van der Waal's forces. Furthermore, these cyclo=dextrin inclusion compounds are stable in solution as well as in solid state, hence their investigation as biomimetic systems. Cyclodextrins and their inclusion compounds have found amazingly diverse uses. The cavities of these cycloamyloses afford protection to hydroperoxides[12], coenzyme A[13] and fatty acids[14]. The cyclohexylamine complex of β-cyclo=dextrin is useful in rust prevention[15] whereas the carbon dioxide clathrate of α-cyclodextrin serves as a baking powder[16]. Large numbers of mono-substituted cyclodextrins have been prepared in connection with enzyme model studies[17]. Current interest in the cycloamyloses arise from their pharmaceutical applications[18].

The zeolites, which are clay minerals, are macromolecular inclusion compounds whose inclusion properties have found wide industrial applica= tions. Zeolites are used to upgrade gasoline, to dry gases on a commercial scale, to separate hydrocarbon mixtures, to act as "carriers" for catalysts to prevent loss of valuable catalytic material during reactions and more commonly as ion exchange media[19]. The zeolites are crystalline structures in which a framework of silicon-oxygen or aluminum-oxygen tetrahedra form the basic structure. They crystallise to provide a three-dimensional network which is permeated with relatively large cavities and channels. These large interstitial spaces normally enclose water molecules. The "holes" which arise on evacuation of the water molecules may be filled by a variety of gas, vapour and straight-chain hydrocarbon molecules. Furthermore the zeolites have stable self-supporting frameworks even in the absence of guest molecules. Besides naturally-occurring zeolites, innumerable types have been synthesised on a tailor-made basis with specified dimensions for selective inclusions.

CLATHRATES

A classical example is the β-hydroquinone clathrate. Powell and his co-workers undertook a comprehensive study of the crystalline nature of the hydroquinone-sulphur dioxide molecular compound by the method of X-ray analysis. They observed the firmness with which the two components were held together even though there appeared to be no strong attractive forces acting between them; that the components were held simply by enclosure of one by the other.

Powell therefore proposed that these compounds be called "clathrates" from the Latin word, *Clathratus* meaning enclosed or protected by cross-bars of a grating[20]. The hydroquinone molecules are linked together through hydrogen bonds between their hydroxyl groups. Six oxygen atoms of six different hydroquinone molecules form a hexagon. Alternating hydroquinone molecules incline upwards and downwards from the hexagon and are further linked in a similar manner through their other hydroxyl group to form a giant molecular structure[1]. The basic framework therefore consists of extended arrays of non-bonded interpenetrating hydroquinone networks which in so doing create cavities. The structure allows for roughly spherical cavities of 4Å in diameter which enclose various guest molecules such as Ar, Kr, Xe, SO_2, CH_3OH, CO_2, HCl and H_2S. Guest molecules which are too large do not yield clathrates and those too small form unstable clathrates. However the cage may distort in order to accommodate various guest species; for example, the elliptical CH_3CN molecules. It has been suggested[21] that a molecule of optimum size which is trapped in the cavity is removed with difficulty due to the appreciable van der Waal's interaction between the guest and host framework.

For more than a century the complexes of water with such simple molecules as chlorine have puzzled chemists. Today, the "gas-hydrates" are a well-known series of clathrate structures. Hydrates are formed with argon, neon, radon, chlorine, methane, ethene and sulphur dioxide. Two crystalline clathrate forms arise. One form, Structure 1, has a cubic cell constant of 12Å and forty-six molecules of water linked together by hydrogen bonds, constitute the unit cell. Eight cavities are formed, two of which are small (5,2Å in diameter) and may accommodate small guest molecules. The remaining six cavities (5,9Å in diameter) can house relatively large molecules.

The second form, Structure 2, has a cubic cell constant of 17Å and one hundred and thirty-six water molecules are associated with each cell. Twenty-four cavities are formed, sixteen small (4,8Å in diameter) and eight relatively large ones (6,2Å in diameter). The maximum composition formulae[22] for Structure 2 may be summarised as follows;

5,7 $H_2O.M_1$ where M_1 is a molecule of the size of methane or hydrogen sulphide (12Å)

7,7 $H_2O.M_2$ where M_2 is a molecule the size of bromine, sulphur dioxide or chlorine (12Å)

46 $H_2O.2M_1.6M_2$ the double hydrate (12Å)

17 $H_2O.M_3$ where M_3 is a molecule the size of propane, methyl iodide or ethyl chloride (17Å)

17 $H_2O.2M_1.M_3$ the double hydrate (17Å).

Dianin's compound has the empirical formula $C_{18}H_{20}O_2$ and is a product of the condensation of phenol and mesityl oxide[23]. This compound has the remarkable ability to tightly retain innumerable organic molecules as well as SO_2, iodine, argon and decalin. The basic feature of this structure is the linking of the hydroxy groups of six molecules by a network of hydrogen bonds such that the oxygen atoms form a distorted hexagon, with alternate molecules of opposite configuration lying on opposite sides of its plane[24]. Two such groups stack so that their bulkier parts interlock forming a cage. The compound is described as having a form somewhat resembling an hourglass which has been cut vertically across the middle of each globe. Strong van der Waal's interactions between one complex unit and its neighbour close the cavity. The guest molecules exhibit disorder and the number of these guest molecules occupying each cavity is dependent on their size. Two small molecules such as ethanol or acetone may accommodate one cage *i.e.* a host to guest ratio of 3:1, while for larger guest species such as benzene or p-xylene, the cage is singly occupied, the ratio then being 6:1.

Clathrate compounds are emerging on the chemical scene to take a place of increasing importance. Their formation is novel, their properties unique and their potential uses very wide.

Clathrate compounds have been extensively applied in the separation of mixtures, in the purification and identification of compounds, and as a means of analysis[25]. The clathration processes are stereoselective and thus chemists are able to separate mixtures into their components even if they do not differ in physico-chemical properties. The only condition for separation is difference in molecular shape and size. Isomers exemplify this situation. Ultra-high purification of particular organic isomers is equally possible[26]. Rare gases have also been effectively separated by selective enclathration[27]. Clathrate chromotography has been used in the separation of isomer mixtures on the analytical scale[28]. The use of clathrates to bring about resolution of racemic mixtures is a new and promising method[9].

An ingenuous use to which clathrate compounds have been put is to enclathrate radioactive or highly toxic material. An example of the former is the inclusion of ^{85}Kr in a hydroquinone cage[29] so that it can be powdered into small crystal dimensions for safe and easy handling. Highly toxic organo-mercurials such as dimethylmercury[30] may be handled with comparative safety in the form of its clathrate with thiachroman, a structural modification of Dianin's compound.

Clathrates may also serve as polymerising agents[31] and as catalysts[32].

It must be emphasised that this short review is merely aimed to provide a workable understanding of the various types of inclusion compounds, their unusual behaviour and their extensive applications. Molecular inclusion compounds have been broadly grouped under the three main headings, layer, channel and clathrate type. Furthermore only selected examples have been briefly discussed.

A more accurate, detailed classification is given by Boeyens[33]. He classifies structures according to the type of intermolecular interactions occurring in the adducts. Thus he divides binary adducts into Addition Complexes and Addition Compounds. Of the former, he sub-classifies Inclusion Complexes and Molecular Complexes. Clathrates (quinol, hydrates) and Channel structures (zeolites, choleic acids, urea) formed as a result of host-host interactions only, are grouped as Inclusion Complexes. Instead Clathrates (Dianin's compound) and Channel structures (cyclodextrins) having host-host and host-guest interactions of equal importance are categorised as Molecular Complexes.

However the divisions are not watertight and gradual transition from one class to another may give rise to an intermediate class. The inclusion compounds formed between inorganic Werner complexes and various organic molecules is such an example. The so-called, Werner Clathrates are by virtue of their name "clathrate", misleading. They are not true clathrates but may be classified as molecular complexes having properties of both the true clathrate and channel type structures.

Interest in these Werner molecular compounds was stimulated by Schaeffer and Dorsey who announced a new method of separation. Their process was described in a science news journal as "Union Oil's New Clathration Process"[34].

Furthermore, the abstract of their first paper presented at the American Chemical Society meeting reads in part as follows,

> "Industrial potentialities for this method may arise in many fields: production of p-xylene or p-cymene for terephthalic acid manufacture, production of m-xylene for isophthalic acid manufacture; recovery of chemicals from coal tar, coal hydrogenation products, petroleum, or shale oil; manipulation of natural products or pharmaceutical intermediates; analytical segregation of fractions of complex mixtures"[1].

Today numerous "clathrates" of the most versatile $Ni(NCS)_2(4\text{-}MePy)_4$ complex have been investigated by the method of X-ray analysis. (The term "clathrate" is used generally to define all crystalline inclusion compounds which have no specific chemical guest-host interactions.)

An essential feature of this Werner complex is the remarkable rotational freedom of the pyridine rings about their Ni - N bonds. The complex is thus able to adjust its molecular shape and in so doing capture guest molecules of different size, shape and polarity. It appears that sorption of a guest molecule has the ability to transform the non-clathrate α-phase $Ni(NCS)_2(4\text{-}MePy)_4$ complex[35]. Transformation of the crystalline α-phase into a stable β-phase occurs in the presence of aromatic hydrocarbons only. In the tetragonal β-phase clathrate, the host lattice is packed so as to provide void space in channel formation. Protruding isothiocyanate groups restrict the channel at various sites producing cavities wherein guest species may be accommodated.

Earlier proposals of guest-host interactions within these clathrates were put forward to account for their selectivity[36]. On the basis of spectral data for a series of clathrates, researchers put forward hypotheses of charge-transfer interactions between host and guest in the clathrate lattice[37]. However recent studies[38,39] have enabled re-interpretation of previous spectral data assuming steric interactions only. No guest-host covalent bonds appear to exist. Thus the only necessary criterion for clathration is that the dimensions of the host "cage" and that of the potential guest be approximately equal.

In order to gain more knowledge as to the physico-chemical behaviour of these clathrates, it is necessary to investigate their crystal structures. A greater understanding of the clathrate formation process will enable the synthesis of new host lattices with specific selectivities towards isomers, enantiomers, conformers, rotamers and isotopomers[2].

CHAPTER 2

CHAPTER 2

GENERAL EXPERIMENTAL AND COMPUTATIONAL PROCEDURES

2.1 THE CHARACTERISATION OF THE COMPOUNDS

The stoicheiometric compositions of the host complexes were determined by microanalytical estimates of their carbon, hydrogen and nitrogen content.

Density measurement, gravimetric analysis, mass spectroscopy, proton nuclear magnetic resonance spectroscopy, thermogravimetric analysis and a nickel content determination were methods employed (where necessary) to identify the "guest" species and to determine the stoicheiometry of the clathrates.

2.2 PRELIMINARY X-RAY ANALYSIS

Single crystals were selected, checked for reflection quality and then sealed in Lindemann capillary tubes with mother liquor (to prevent deterioration in air *i.e.* guest desorption). A two-circle optical goniometer was used for the initial alignment. Oscillation photography provided the final, precise crystal alignment.

Oscillation and Weissenberg (zero layer and upper layer) photographs were taken using a non-integrating Stoe (Heidelberg) goniometer attached to a camera of radius 28,65mm. Ni-filtered CuK$_\alpha$ radiation (λ = 1,5418Å) was used. The X-ray generators, models Philip PW 1120 and PW 1008, were operated at 0,8kW (20mA and 40kV). X-ray films (3M) were processed in the usual manner with Kodak X-ray developer and fixer solutions.

Unit cell dimensions and space group symmetries were determined from the photographs.

2.3 DIFFRACTOMETER DATA COLLECTION

Suitable crystals mounted in Lindemann capillary tubes with mother liquor were sent to Mr J. Albain at the National Physical Research Laboratory, C.S.I.R. (Pretoria) for a diffractometer data collection.

The relative intensities of the reflections were measured on a Philips PW 1100 computer-controlled four-circle diffractometer. A Philips PW 1130 X-ray generator, operating at 1kW (20mA and 50kV) provided graphite monochromated MoK_α radiation ($\lambda = 0{,}7107\text{Å}$).

Accurate cell parameters were obtained (at room temperature) by a least squares analysis of the χ, ϕ and 2θ angles of 25 standard reflections accurately centred on the diffractometer. The three-dimensional intensity data were then collected employing the ω-2θ scan technique[40].

To ensure instrumental stability and to monitor any crystal decomposition, the intensities of three reference reflections were measured at approximately hourly intervals throughout the duration of the data collection. Reflections were considered "present" (observed) if I_{rel} exceeded $2\sigma I_{rel}$. The standard error σI_{rel} in the relative integrated intensity, I_{rel}, was calculated as follows:

$$\sigma I_{rel} = \left[N_{pk} + N_{bg} + N_{instr}\right]^{\frac{1}{2}}$$

where,

N_{pk} = gross peak count for a specific reflection

N_{bg} = background count as measured on either side of the peak

N_{instr} = $[0{,}02(N_{pk} - N_{bg})]^2$

Lorentz-polarisation corrections were automatically applied to all reflection data.

2.4 COMPUTATION

All computations were performed on a Univac 1106 computer system at the computer centre of the University of Cape Town.

The program SHELX76[41] was used for crystallographic data reduction, structure solution and refinement. Features of the program which were utilised include data reduction, full-matrix least squares refinements, geometric positioning and constrained refinement of the hydrogen atoms, analysis of variance and automatic optimisation of weighting schemes, fourier syntheses with peak search and structure factor listings.

The agreement between observed (F_o) and calculated (F_c) structure factors is expressed by the conventional residual index R[42] defined as

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

or expressed as

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

where $\omega = k/[\sigma^2(F) + gF^2]$ upon introduction of a weighting scheme. k was redetermined after each structure factor calculation. The value of g was chosen to give smallest variation of $\omega\Delta^2$ with the magnitude of F_c.

An analysis of variance computed after the final refinement cycle gives an indication of the effectiveness of the weighting scheme. A resulting low value for the discrepancy index R (<10%) is indicative of a correctly refined structure.

Atomic radii used were those of Pauling[43]. Scattering factors for all non-hydrogen atoms were from Cromer and Mann[44] and those for the hydrogen atoms from Stewart *et al*[45].

The program XANADU[46], enabled geometric positioning of hydrogen atoms and calculation of bond distances, bond angles, torsion angles and least squares planes.

The program PLUTO[47] was used for the plotting of individual molecules and molecules in crystalline arrangement.

The potential energy environment of a molecule in a crystal was conveniently studied using the program EENY[47].

CHAPTER 3

CHAPTER 3

THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(ISOTHIOCYANATO)BIS(4-METHYL=PYRIDINE)BIS(4-PHENYLPYRIDINE)NICKEL(II).METHYL CELLOSOLVE (PYRID)

3.1 EXPERIMENTAL AND CHARACTERISATION

Synthesis

The host complex, $Ni(NCS)_2(4\text{-}MePy)_4$, was prepared by the method of Schaeffer *et al*[48] with minor variation as follows;
6,39g (0,084mole) of ammonium thiocyanate was added to a solution of 10,00g (0,042mole) of nickel chloride hexahydrate in 100ml of water. 16,45ml (0,168mole) of 4-methylpyridine (4-MePy) was slowly added with constant stirring. A blue precipitate formed and the mixture was stirred for an additional 20 minutes and then filtered. The blue residue, the host complex, was air-dried for 24 hours. The entire operation was carried out at room temperature.

Formation of the clathrate involved dissolving 2,19g (0,004mole) of solid Werner complex and 0,4ml (0,004mole) of 4-methylpyridine in 4ml of the solvent methyl cellosolve, by heating to 108°C. To this hot solution 2,33g (0,015mole) of the chosen guest, 4-phenylpyridine, was slowly added. Crystallisation of the (unexpected $Ni(NCS)_2(4\text{-}MePy)_2(4\text{-}PhPy)_2$. Methyl Cellosolve) clathrate occurred after 6 days standing at room temperature. The light-blue monoclinic-shaped crystals were kept sealed under mother liquor to prevent deterioration (desorption of the guest species) in air.

Analyses

Mass Spectroscopy

The application of mass spectroscopy provided a quick, accurate means whereby the guest species in the clathrate could be identified.

The guest, although enclosed in its "cage", is not chemically bonded to the host network. It is likely therefore to be preferentially volatilised and ionised. The total ion current spectrum revealed two distinct peaks (See Figure 3.1). The fragmentation pattern obtained at scan number 27 is indicative of guest breakdown, whereas the fragments in the pattern at scan number 52 are related to the host structure. Table 3.1 presents the mass spectrum (in tabulated form) with proposed fragmentational assignments.

The guest species was unambiguously identified as the solvent methyl cellosolve (2-methoxyethanol).

Of great interest was the presence of the m/e = 155 peak in the fragmentation pattern at the higher scan number. It was then obvious that apart from the 4-methylpyridine ligands (m/e = 93), the host also contained 4-phenylpyridine ligands (m/e = 155). Furthermore the intensity of the 155 peak was much lower than that of the 93 peak. A simple explanation is the greater stability of a phenyl radical as opposed to that of a methyl radical. The 4-phenylpyridine ligands are thus readily fragmented, hence the low intensity of the m/e = 155 peak.

The mass spectrum was recorded on a V.G. Micromass F16 spectrometer operating at 70eV.

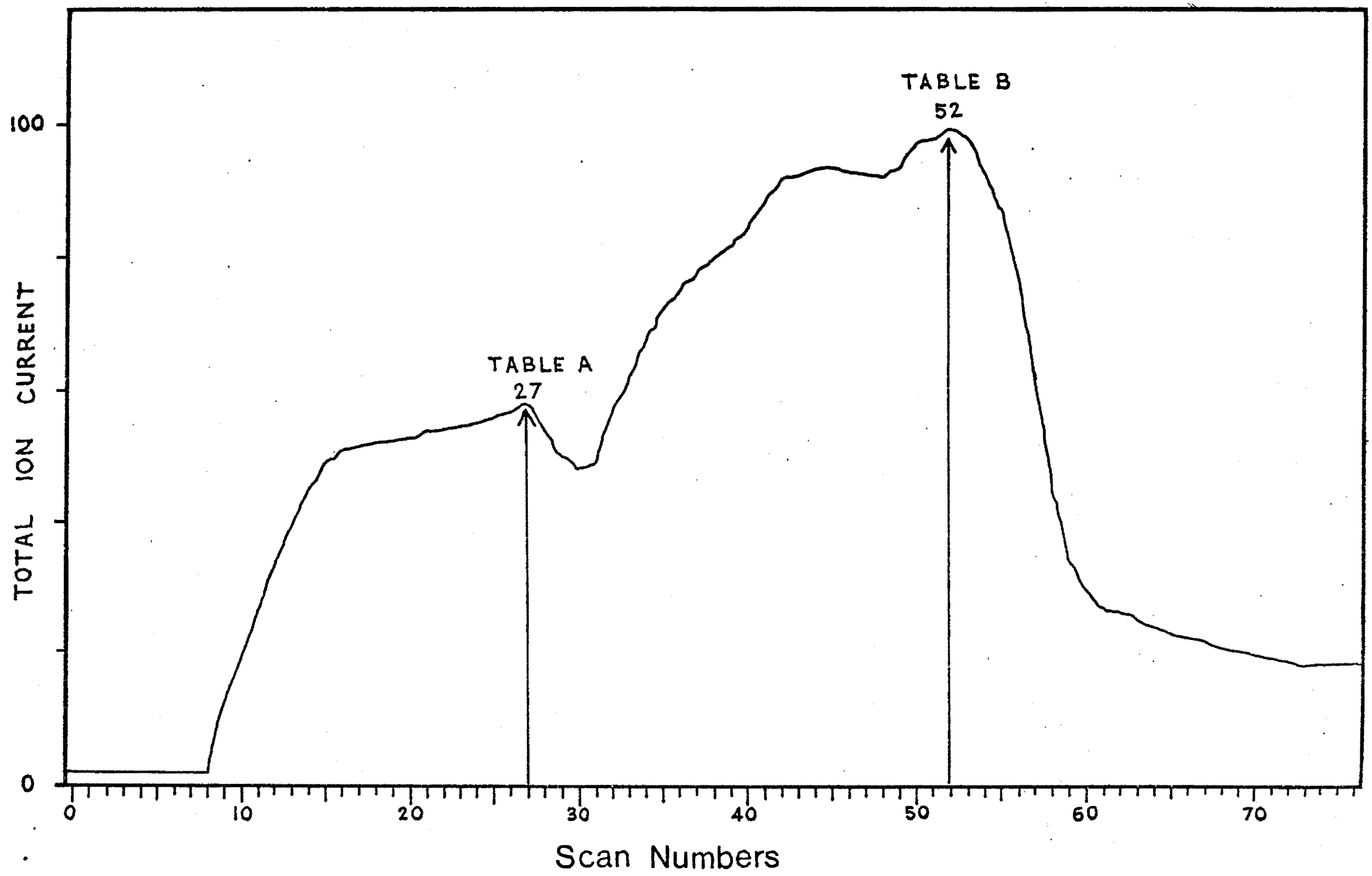


FIGURE 3.1 The Total Ion Current Spectrum for the PYRID clathrate.

TABLE 3.1 MASS SPECTRUM FOR PYRID

m/e	Relative % Abundance	Possible Inference
Table A (Guest)		
28	53	N_2^+
31	17	CH_3O^+
32	13	O_2^+
45	100	$C_2H_5O^+$
58	4	$C_3H_6O^{+\bullet}$
76	8	$C_3H_8O_2^{+\bullet}$
Table B (Host)		
28	47	N_2^+
39	24	$C_3H_3^+$
51	9	$C_4H_3^+$
65	21	$C_5H_5^+/C_4H_3N^+$
66	37	$C_4H_4N^+$
78	5	$C_5H_4N^+$
92	23	$C_6H_6N^+$
93	100	$C_6H_7N^+$
155	7	$C_{11}H_9N^+$

Gravimetric Analysis

In order to determine the guest to host molar ratio it was necessary to calculate the stoicheiometric amount of guest present in the clathrate.

A sample of clathrate crystals (A) was submitted for microanalysis. A second sample (A') (from the same batch of crystals) was dabbed free of mother liquor and weighed on a microbalance, *i.e.* a six place balance (the weight remaining constant over a 15 minute period). This sample was then placed in a vacuum pump operating at 50°C with a pressure of 0,5 - 1 mmHg for one hour in order to desorb the more volatile methyl cellosolve guest molecules (bp_{20} 34 - 41°C).

The desorbed clathrate sample (B') was then reweighed (the weight remaining constant) and immediately analysed for carbon, hydrogen and nitrogen content. Special precautions, *i.e.* wrapping the crystals in a foil boat, ensured protection of the crystals from the atmosphere during transfer to and from the balance and vacuum pump.

Initial weight of sample	= 3,022mg
Final weight (after 1 hour in the vacuum pump)	= 2,690mg
Weight loss	= 0,332mg (10,98%)

Assuming the weight loss equivalent to the guest content in the clathrate, the guest to host molar ratio was determined as 1,08 : 1.

Microanalysis

The initial host complex $Ni(NCS)_2(4\text{-}MePy)_4$ was analysed for percentage carbon, hydrogen and nitrogen content.

	%C	%H	%N
Calculated	57,05	5,16	15,35
Found	57,15	5,10	15,25

The batch of clathrate crystals (A) submitted for analysis produced the following results.

	%C	%H	%N
Found	62,15	5,45	11,25

The sample analysed after desorption of guest (B') (the empty host complex) had the following elemental content.

	%C	%H	%N
Found	63,95	4,80	12,50

The theoretical carbon, hydrogen and nitrogen content of the complex, $Ni(NCS)_2(4\text{-}MePy)_2(4\text{-}PhPy)_2$, calculated as 64,39%, 4,80% and 12,52% respectively, corresponds closely to the measured values of the B' sample. This confirms the host complex to be $Ni(NCS)_2(4\text{-}MePy)_2(4\text{-}PhPy)_2$.

We then proposed that the difference in percentage carbon, hydrogen and nitrogen content between sample A and sample B' corresponds to the percentage elemental content of the guest, methyl cellosolve, (*i.e.* $\Delta\%C = 1{,}80$, $\Delta\%H = 0{,}65$ and $\Delta\%N = 1{,}25$).

Theoretical changes in the percentage carbon, hydrogen and nitrogen content after guest desorption were calculated assuming various guest to host molar ratios as follows;

Guest to Host Molar Ratio	Δ%C	Δ%H	Δ%N
1 : 1	1,73	0,59	1,28
1,5 : 1	2,47	0,85	1,83
2 : 1	3,14	1,07	2,32

The measured changes calculated above correspond closely to the theoretical 1 : 1 guest to host molar ratio thereby confirming the composition of the clathrate as such.

Density Determination

The crystal density was determined as 1,28gcm^{-3} by flotation in a mixture of saturated potassium iodide and water. Assuming a 1 : 1 guest to host molar ratio, the number of host molecules in the unit cell was calculated to be 4. (Crystal structure analysis confirmed the number of molecules per unit cell as 4.)

The density measurement (D_m) also provided a quantitative estimate of the guest to host molar ratio. From the equation,

$$Z_H(M_H) + Z_G(M_G) = ND_m abc\sin\beta \times 10^{-24}$$

where,

$Z_H = 4$: Number of host molecules per unit cell

$M_H = 671{,}524$: Molecular weight of host in gmol^{-1}

$M_G = 76{,}09$: Molecular weight of guest in gmol^{-1}

$N = 6{,}023 \times 10^{23}$: Avogadro constant

D_m = 1,28(±0,02) : Measured density in gcm^{-3}

$abc\sin\beta$ = 3952,08(±3,4) : Volume of unit cell in Å^3

Z_G, the number of guest molecules in the unit cell was calculated to be 4,74(±0,07). The guest to host molar ratio was determined as 1,19(±0,02) : 1.

Kemula *et al*[49] claim that quantitative analysis is generally of low accuracy when the guest species is an aliphatic compound of low molecular weight.

However the results obtained by these various methods correlated sufficiently well for us to safely determine the guest to host molar ratio as 1 : 1.

3.2 PRELIMINARY X-RAY ANALYSIS

A monoclinic space group was revealed by oscillation and Weissenberg photography. The approximate cell parameters obtained from the photographs were; a = 11,15Å, b = 22,72Å, c = 15,85Å, β = 98° and Z = 4.

From the Weissenberg photographs, the conditions for non-extinction of reflections were determined as

hkl : $h + k = 2n$

$h0l$: $l = 2n$ ($h = 2n$)

$0k0$: $k = 2n$

These systematic absences are indicative of the space groups C_c or $C_2/_c$[50].

3.3 INTENSITY DATA COLLECTION

The diffractometer data set contained 2818 reflections collected within the range $6^{\circ} < 2\theta < 46^{\circ}$. 200 were excluded as systematically absent and a further 591 were omitted as they did not satisfy the criterion $I_{rel} > 2\sigma I_{rel}$ for an observed reflection. The remaining 2026 reflections constituted the "observed" data.

The three reference reflections were measured every 107 reflections and their intensities remained constant to within 0,65% of their mean value. Accurate cell parameters determined by least squares analysis and other relevant crystal data are listed in Table 3.2.

TABLE 3.2 CRYSTAL DATA

Molecular formula	$C_{39}H_{40}N_6NiO_2S_2$
Molecular weight	747,614gmol^{-1}
Space group	$C2/c$
a	10,648(5)Å
b	23,005(12)Å
c	16,294(8)Å
β	98,04(2)$^{\circ}$
V	3952,08Å^3
D_m	1,28gcm^{-3}
D_c	1,26gcm^{-3}
$\mu(MoK_{\alpha})$	5,87mm^{-1}
$F(000)$	1568
Crystal dimensions	0,63 x 0,38 x 0,15mm
Scan mode	ω-2θ
Scan width	0,60$^{\circ}\theta$
Scan speed	0,02$^{\circ}\theta$s^{-1}

3.4 SOLUTION AND REFINEMENT OF THE CLATHRATE STRUCTURE

3.4.1 THE HOST COMPLEX, $Ni(NCS)_2(4\text{-}MePy)_2(4\text{-}PhPy)_2$.

Solution was initially attempted in the non-centrosymmetric space group C_c. A three-dimensional Patterson vector map was computed in order to locate the coordinates of the nickel atom. In addition, a vector grid for the space group C_c was constructed wherefrom vector coordinates were derived. The result of this is that for the nickel atom located at the general position x, y, z, the Ni x Ni vectors are;

Vector Position	Multiplicity
0, 0, 0	4
½, ½, 0	4
0, $2y$, ½	2
0, $-2y$, ½	2
½, ½+$2y$, ½	2
½, ½-$2y$, ½	2

Thus the Patterson will only yield the y coordinate of the nickel atom and since in C_c the origin is on the c glide plane, we arbitrarily fixed the x and z coordinates of the nickel atom at 0. The nickel coordinates were thus established as 0, 0,1719, 0.

A weighted electron density difference map based on the nickel atom further revealed thirty-seven non-hydrogen atoms with the conventional R factor equal to 0,42. All these atoms were inserted and in the subsequent elctron density calculation the remaining seven non-hydrogen atoms were located substantially lowering the R value to 0,19.

Although the E statistics implied a centrosymmetric space group we paid them scanty attention as the presence of a heavy atom generally decreases the reliability of the E statistical values.

However, having located all the host atoms we observed that the host molecule was directly aligned along a two-fold axis parallel to b. The non-centrosymmetric space group C_c had therefore to be replaced by the centrosymmetric $C_2/_c$ equivalent. With only four molecules per unit cell, the nickel atoms lie at special positions. Furthermore the host molecule displayed two-fold axial symmetry, hence it must be located at the Wyckoff position e in the $C_2/_c$ space group. The appropriate vector grid was then constructed and the various vector types derived are identical to those derived previously for the C_c space group. The y coordinate of the nickel atoms was thus confirmed as 0,1719. The x and z coordinates were fixed at 0 and 0,25 respectively.

The newly established nickel coordinates (0, 0,1719, 0,25) and half the host atoms (*i.e.* the asymmetric unit) were then inserted into a structure factor calculation and least squares refinement which yielded an R equal to 0,17.

Anisotropic temperature factors were calculated for the nickel atom (from tables listed by Peterse and Palm[51]) and included in the following least squares refinement, reducing R to 0,13. Finally the sulphur atom was treated anisotropically.

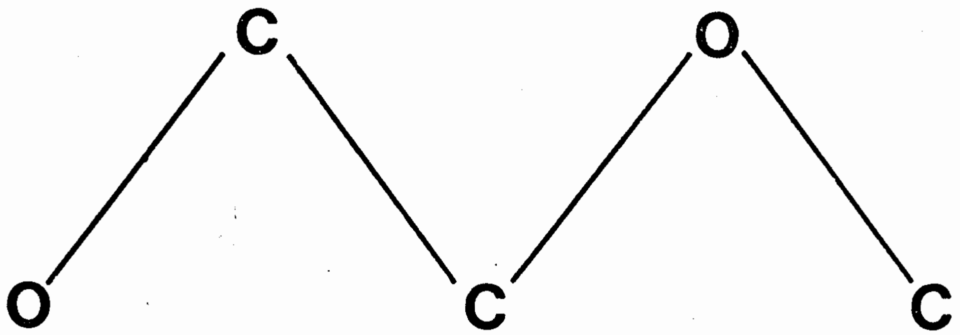
The host molecule was thus successfully refined, but the positions of the guest atoms could not be satisfactorily established.

3.4.2 LOCATION OF THE GUEST, METHYL CELLOSOLVE ($C_3H_8O_2$)

Instead maps of electron density were computed at intervals of y = 0,02. A search revealed high concentration of electron density in the two-dimensional slice at y = 0,5. This electron-rich region was contoured at intervals of 0,2eÅ^{-3} as shown in Figure 3.2.

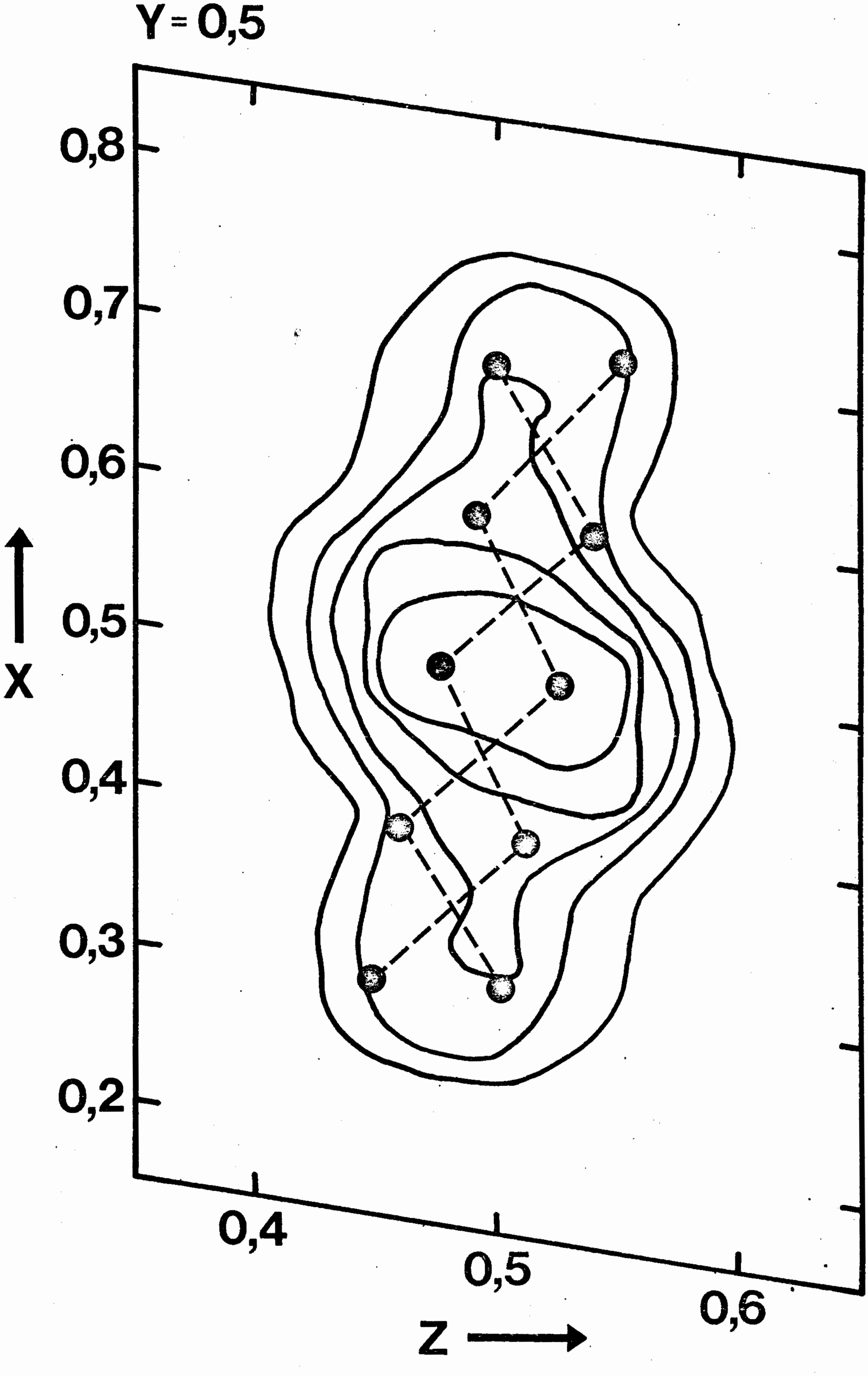
An accurate model of the guest molecule, methyl cellosolve, was fitted to the contoured electron density region with much patient effort. This was achieved by means of "shadowing". A spot-light some distance away illuminated the stick model so that its shadow fell precisely within the contour lines in the most favourable orientation.

A further complication arose. Symmetry consideration required the guest molecule to lie on a centre of inversion and because the molecule is not centrosymmetric, statistical disorder was invoked. Neglecting hydrogen atoms, the guest molecule is

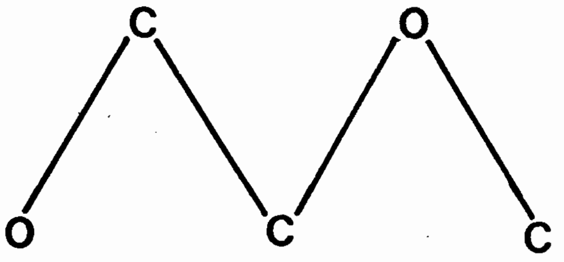


and was further simplified by standardising all the bond lengths to ∿1,5Å and bond angles to ∿110°. This was achieved employing the program XANADU. The resolution in the electron density map was poor so there were two equally probable modes of locating the molecule;

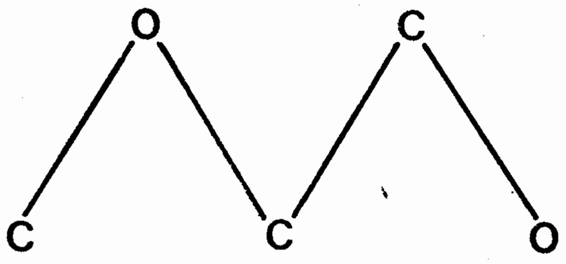
FIGURE 3.2 A two-dimensional electron density map.



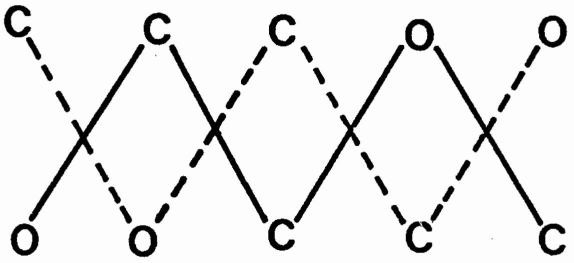
i.e.



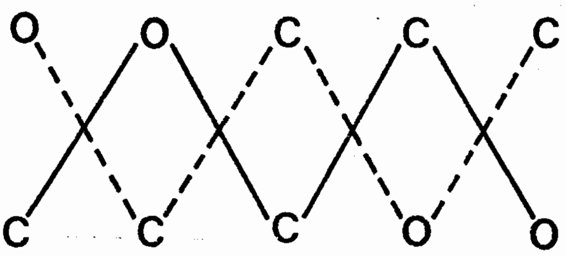
or



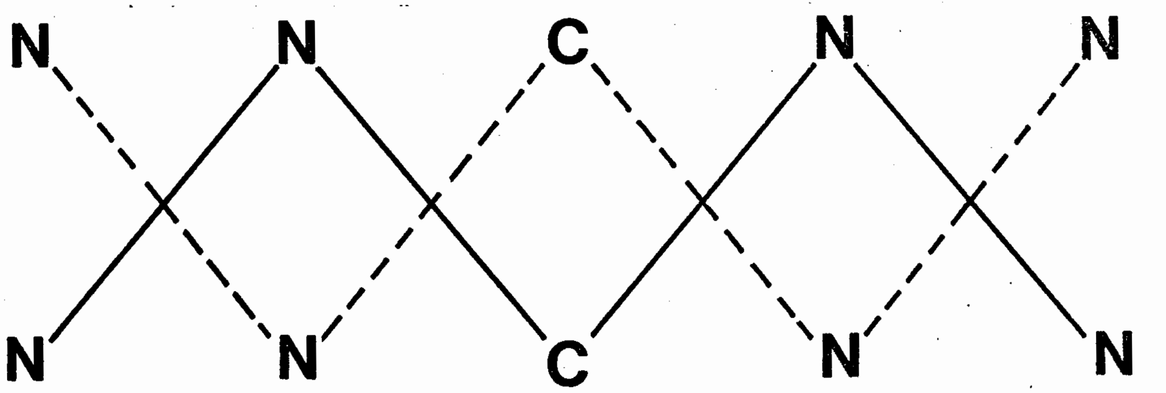
The following orientations are obtained by addition of the centre of inversion,



or



these combine to



The average atomic scattering factors of the carbon and oxygen atoms were approximated as the atomic scattering factor of the nitrogen atom.

i.e. $[f(\mathrm{C}) + f(\mathrm{O})]/2 = f(\mathrm{N})$

The positions of the five atoms in one molecular orientation were pin-pointed and their coordinates estimated. These coordinates were inserted into the SHELX76 program with site occupancy factors fixed to 0,5. The five guest atoms were then fixed at these positions.

All the host hydrogen atoms including those already revealed were constrained to ride at 1,08Å from their parent carbon atoms, their positions dictated by the molecular geometry. No attempt was made to include the hydrogen atoms of the guest molecules in the final model of the crystal structure.

The final least squares refinement which included the host non-hydrogen and hydrogen atoms and the guest non-hydrogen atoms, converged to $R = 0{,}12$; $R_\omega = 0{,}14$ with the weighting scheme $\omega = (\sigma^2 F + 0{,}002F^2)^{-1}$.

The analysis of variance (Table 3.3) computed after the final cycle showed that this weighting scheme was satisfactory. In the final cycle of refinement the mean standard deviation in the parameters was greater than 50 times the average shift which indicated satisfactory convergence.

The final atomic coordinates with corresponding thermal motion parameters are listed in Table 3.4. Lists of observed and calculated structure factors are presented in Appendix 1.

TABLE 3.3 ANALYSIS OF VARIANCE

---

a) By parity groups

Group	*ggg*	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*	All
N	545	0	0	513	466	0	0	502	2026
V	608	0	0	540	482	0	0	541	547

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

$\sin\theta$	0,00-0,18	0,18-0,22	0,22-0,25	0,25-0,28	0,28-0,30	0,30-0,32	0,32-0,34	0,34-0,36	0,36-0,38	0,38-0,40
N	248	178	194	274	199	200	196	218	228	91
V	863	595	507	602	555	496	414	376	338	304

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

$\surd(F/F_{max})$	0,00-0,16	0,16-0,18	0,18-0,20	0,20-0,22	0,22-0,24	0,24-0,26	0,26-0,29	0,29-0,32	0,32-0,39	0,39-1,00
N	252	228	212	214	183	178	196	158	203	202
V	539	560	547	541	558	550	503	678	520	485

d) As a function of |Miller index|

$\lvert h \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	141	276	264	256	243	217	197	150	118	96	48	20	0	0	0
V	909	669	566	546	464	501	412	411	393	403	313	246	0	0	0

TABLE 3.3 CONT/....

TABLE 3.3 CONTINUED

$\|k\|$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	76	141	123	108	124	123	90	107	125	111	108	119	100	72	499
V	575	537	568	724	694	511	698	482	436	525	572	463	404	587	504

$\|l\|$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	93	156	180	166	173	162	169	148	145	124	116	102	90	65	137
V	753	647	652	579	628	463	555	447	461	529	410	404	526	421	493

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 (Å x 10^4) AND ISOTROPIC THERMAL MOTION PARAMETERS ($Å^2$ x 10^3) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom (Host)	*x/a*	*y/b*	*z/c*	U_{iso}
Ni(1)	0(0)	1721(1)	2500(0)	a
N(1)	1704(8)	1718(4)	3238(6)	50(2)
C(1)	2546(10)	1692(5)	3781(7)	50(3)
S(1)	3704(4)	1690(2)	4543(3)	a
N(11)	0(0)	795(6)	2500(0)	53(3)
C(12)	-1079(11)	487(5)	2478(7)	54(3)
C(13)	-1131(11)	-118(5)	2472(7)	59(3)
C(14)	0(0)	-446(7)	2500(0)	50(4)
C(111)	0(0)	-1066(7)	2500(0)	59(4)
C(112)	-834(15)	-1384(7)	2893(9)	84(4)
C(113)	-865(15)	-1995(7)	2907(9)	87(4)
C(114)	0(0)	-2272(12)	2500(0)	107(8)
N(21)	-954(8)	1721(4)	3574(5)	48(2)
C(22)	-395(25)	1623(9)	4302(15)	134(7)
C(23)	-1031(25)	1601(10)	5032(18)	148(8)
C(24)	-2277(13)	1657(5)	4969(9)	67(4)
C(25)	-2864(15)	1766(6)	4204(9)	83(4)
C(26)	-2180(15)	1806(6)	3533(10)	84(4)
C(27)	-2960(16)	1598(7)	5688(10)	91(5)
N(31)	0(0)	2658(5)	2500(0)	50(3)
C(32)	589(10)	2963(5)	3144(7)	51(3)
C(33)	614(12)	3540(6)	3159(8)	61(3)
C(34)	0(0)	3882(8)	2500(0)	67(5)

TABLE 3.4 CONT/....

TABLE 3.4 CONTINUED

Atom (Host)	*x/a*	*y/b*	*z/c*	U_{iso}
C(311)	0(0)	4518(8)	2500(0)	69(5)
C(312)	31(16)	4811(8)	1809(12)	105(5)
C(313)	53(20)	5497(11)	1777(15)	153(8)
C(314)	0(0)	5716(15)	2500(0)	144(11)
H(12)	-1952(11)	727(5)	2464(7)	b
H(13)	-2032(11)	-338(5)	2450(7)	b
H(112)	-1491(15)	-1149(7)	3219(9)	b
H(113)	-1514(15)	-2243(7)	3222(9)	b
H(114)	0(0)	-2741(13)	2500(0)	b
H(22)	610(25)	1532(9)	4378(15)	b
H(23)	-486(25)	1537(10)	5636(18)	b
H(25)	-3861(15)	1874(6)	4114(9)	b
H(26)	-2713(15)	1902(6)	2934(10)	b
H(271)	-3952(16)	1713(7)	5571(10)	c
H(272)	-2540(16)	1783(7)	6272(10)	c
H(273)	-2866(16)	1131(7)	5714(10)	c
H(32)	1066(10)	2730(5)	3674(7)	b
H(33)	1110(12)	3766(6)	3689(8)	b
H(312)	32(16)	458(8)	1232(12)	b
H(313)	76(20)	5343(11)	1153(15)	b
H(314)	0(0)	5247(16)	2500(0)	b
Atom (Guest)				
N(91)	3000(0)	4400(0)	4450(0)	d
N(92)	4000(0)	4650(0)	5130(0)	d

TABLE 3.4 CONT/....

TABLE 3.4 CONTINUED

Atom (Guest)	*x/a*	*y/b*	*z/c*	U_{iso}
C(93)	5000(0)	5000(0)	4750(0)	d
N(94)	6000(0)	5250(0)	5400(0)	d
N(95)	6950(0)	5600(0)	5000(0)	d

---

[a] Anisotropic thermal parameters of the form:

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

with parameters

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni(1)	39(1)	46(1)	37(1)	0(0)	-3(1)	0(0)
S(1)	70(3)	165(5)	69(3)	4(3)	-24(2)	1(3)

[b] All H atoms have U_{iso} = 152(18)

[c] All H atoms have U_{iso} = 103(23)

[d] All atoms have U_{iso} = 297(10)

3.5 DESCRIPTION OF THE CLATHRATE STRUCTURE

3.5.1 MOLECULAR STRUCTURE

A perspective view of the host complex is shown in Figure 3.3. The host molecule is positioned on a crystallographic two-fold axis, the atomic nomenclature is therefore self-explanatory. Intramolecular bond lengths and angles are listed in Tables 3.5 and 3.6 respectively.

The nickel atom is octahedrally coordinated to the nitrogen atoms of the two isothiocyanate ligands, the two 4-methylpyridine ligands and the two 4-phenylpyridine ligands. There is a significant difference between the Ni - N bond distances of the isothiocyanate and pyridine ligands. Ni - N bond lengths for the isothiocyanate ligands are 2,03Å whereas the average Ni - N distances for the pyridine ligands are 2,14Å. This inequivalence may be due to intramolecular repulsion between the isothiocyanate groups and the pyridine ligands resulting in the lengthening of the Ni - N (pyridine) distances. By virtue of molecular two-fold axial symmetry the nickel atom is positioned directly in the N(11), N(21), N(31) and N(41) molecular plane. Angles subtended at the nickel atom are all within 0,5° of 90°. (Figure 3.4 clearly depicts the environment of the nickel atom including the isothiocyanate ligands.)

The isothiocyanate ligands are not linear. The Ni - N - C angles are 167,0(8)°. This significant deviation from linearity at the nitrogen atom is a characteristic feature observed in all previous study.

The *trans* 4-phenylpyridine ligands lie directly on the two-fold axis. Individual 4-phenylpyridine ligands have essentially planar aromatic rings. The equations of the least squares mean planes and atomic deviations

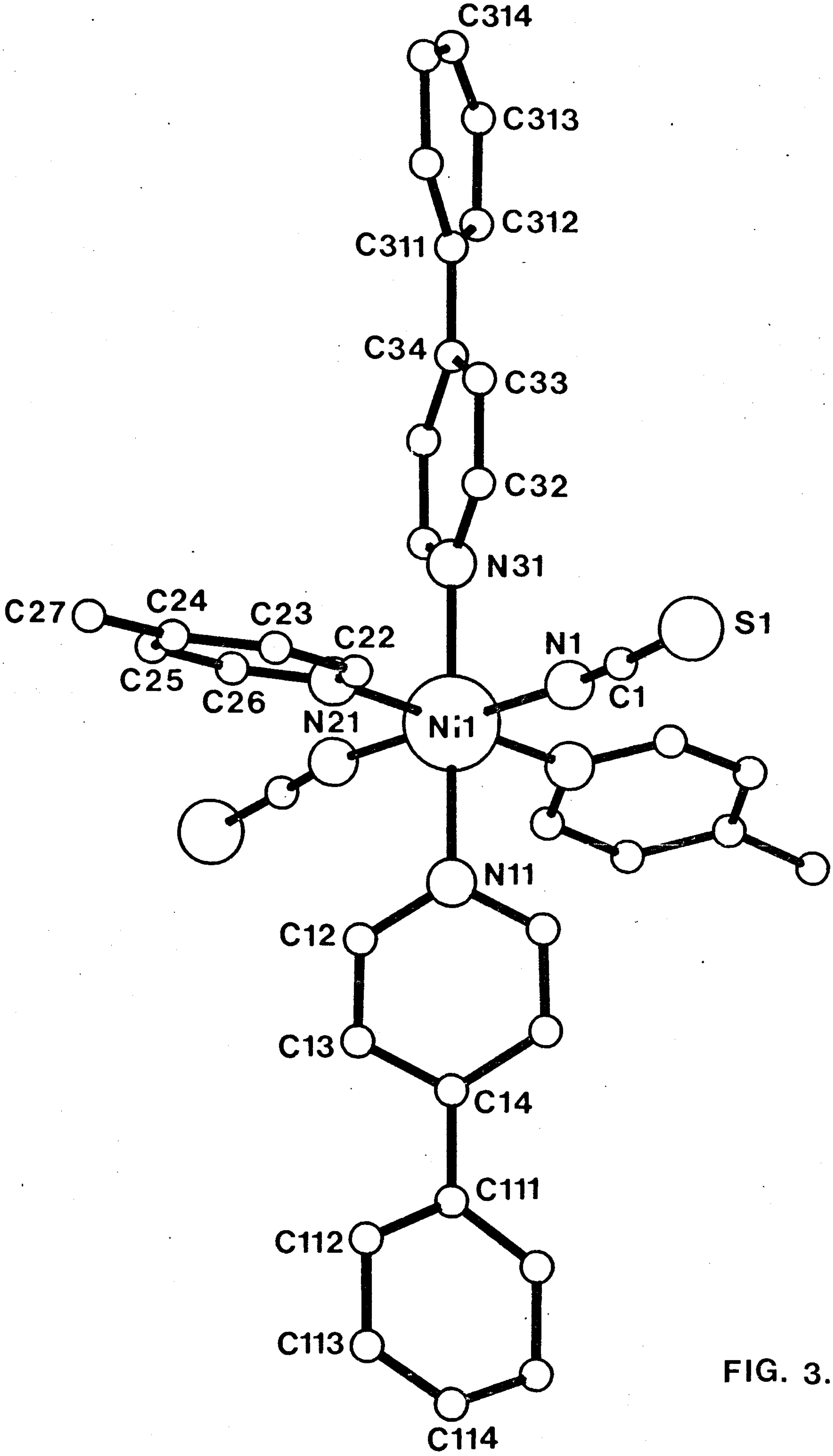

C314
C313
C312
C311
C34
C33
C32
N31
C27
C24
C23
C22
C25
C26
N21
N1
S1
C1
Ni1
N11
C12
C13
C14
C111
C112
C113
C114

FIG. 3.3 .

TABLE 3.5 BOND LENGTHS (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Host molecule

Ni(1) - N(1)	2,032(8)
Ni(1) - N(11)	2,131(12)
Ni(1) - N(21)	2,142(8)
Ni(1) - N(31)	2,155(11)
N(1) - C(1)	1,170(13)
C(1) - S(1)	1,622(10)
N(11) - C(12)	1,346(12)
C(12) - C(13)	1,393(14)
C(13) - C(14)	1,416(13)
C(14) - C(111)	1,428(21)
C(111) - C(112)	1,376(16)
C(112) - C(113)	1,406(20)
C(113) - C(114)	1,366(17)
N(21) - C(22)	1,271(22)
N(21) - C(26)	1,313(15)
C(22) - C(23)	1,450(29)
C(23) - C(24)	1,322(25)
C(24) - C(25)	1,338(18)
C(24) - C(27)	1,469(19)
C(25) - C(26)	1,398(19)
N(31) - C(32)	1,342(11)
C(32) - C(33)	1,329(15)
C(33) - C(34)	1,414(14)
C(34) - C(311)	1,463(24)
C(311) - C(312)	1,318(18)

TABLE 3.5 CONT/....

TABLE 3.5 CONTINUED

Host molecule	
C(312) - C(313)	1,579(25)
C(313) - C(314)	1,289(24)
Guest molecule	
N(91) - N(92)	1,537(0)
N(92) - C(93)	1,533(0)
C(93) - N(94)	1,507(0)
N(94) - N(95)	1,510(0)
All C - H bond lengths[a]	1,08

---

[a] Bond lengths fixed

TABLE 3.6 BOND ANGLES (DEGREES) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Host Molecule

N(1) - Ni(1) - N(11)	89,8(2)
N(1) - Ni(1) - N(21)	90,2(3)
N(1) - Ni(1) - N(31)	90,2(2)
N(11) - Ni(1) - N(21)	90,0(2)
N(21) - Ni(1) - N(31)	90,0(2)
Ni(1) - N(1) - C(1)	167,0(8)
N(1) - C(1) - S(1)	177,3(9)
Ni(1) - N(11) - C(12)	121,8(6)
N(11) - C(12) - C(13)	124,1(10)
C(12) - C(13) - C(14)	119,8(10)
C(13) - C(14) - C(111)	122,1(7)
C(14) - C(111) - C(112)	122,1(8)
C(111) - C(112) - C(113)	123,8(13)
C(112) - C(113) - C(114)	116,1(16)
Ni(1) - N(21) - C(22)	123,3(12)
Ni(1) - N(21) - C(26)	122,7(8)
C(22) - N(21) - C(26)	114,0(14)
N(21) - C(22) - C(23)	124,1(21)
C(22) - C(23) - C(24)	120,7(22)
C(23) - C(24) - C(25)	115,1(16)
C(23) - C(24) - C(27)	122,1(16)
C(27) - C(24) - C(25)	122,8(13)
C(24) - C(25) - C(26)	120,9(14)
C(25) - C(26) - N(21)	125,0(13)
Ni(1) - N(31) - C(32)	121,5(6)

TABLE 3.6 CONT/....

TABLE 3.6 CONTINUED

Host molecule	
N(31) - C(32) - C(33)	122,8(10)
C(32) - C(33) - C(34)	122,4(11)
C(33) - C(34) - C(311)	123,8(7)
C(34) - C(311) - C(312)	120,8(10)
C(311) - C(312) - C(313)	122,8(16)
C(312) - C(313) - C(314)	110,0(22)
Guest Molecule	
N(91) - N(92) - C(93)	110,8(0)
N(92) - C(93) - N(94)	112,3(0)
C(93) - N(94) - N(95)	110,5(0)

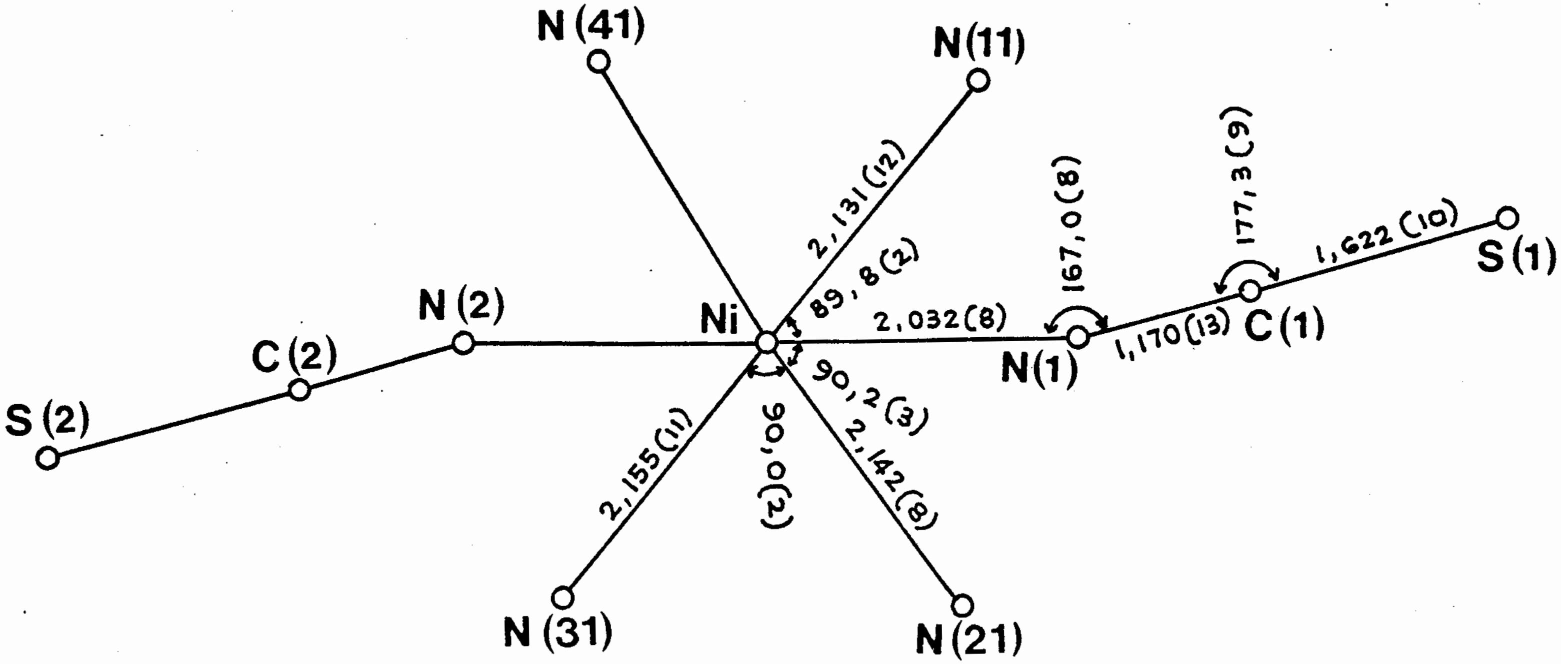


FIGURE 3.4 The environment of the nickel atom including the isothiocyanate ligands. Distances (Å) and angles (°) are shown for the asymmetric unit only.

therefrom are listed in Table 3.7. The phenyl-moieties of these ligands are planar to within 0,01Å. The pyridine-moieties show minimal distortion, in particular the N(31) pyridine ring which is planar to within experimental error. The aromatic rings in the individual ligand are not coplanar. The C(111) phenyl ring is twisted 35° out of the plane of the N(11) pyridine ring whereas the C(311) phenyl moiety is twisted 33° with respect to the N(31) pyridine ring. The phenyl rings of the 4-phenylpyridine ligands are positioned well above the crowded N(11), N(21), N(31) and N(41) molecular plane. They experience greater vibrational freedom hence their higher isotropic thermal motion parameters.

The *trans* 4-methylpyridine ligands are twisted 31° with respect to each other. Individual pyridine rings are planar to within 0,01Å.

An essential feature of the $Ni(NCS)_2(4\text{-}MePy)_2(4\text{-}PhPy)_2$ complex is the conformational freedom of the pyridine ligands which rotate about their respective Ni - N bonds. Not only is rotation necessary to eliminate unfavourable intramolecular steric interaction but essential in order to adjust molecular shape and in so doing make clathration of various guests possible.

3.5.2 MOLECULAR PACKING

An illustration of the packing of the centrosymmetric host molecules in the unit cell is shown in projection down the x axis. (See Figures 3.5 and 3.6)

The host molecules lie on a two-fold axis. They pack in repetitive up-down patterns. Viewing down the x axis, each host molecule has a "head"

TABLE 3.7 LEAST-SQUARES PLANES AND TORSION ANGLES

---

1 (a) Equations of least-squares planes are expressed in orthogonalised space as $pX + qY + rZ = S$.

Plane 1 : The pyridine ring atoms (N(21), C(22), C(23), C(24), C(25), C(26))

$1{,}8912X + 22{,}1975Y + 2{,}7164Z = 4{,}6042$

Plane 2 : The pyridine ring atoms (N(31), C(32), C(33), C(34), C(35), C(36))

$9{,}6577X + 0{,}0Y - 8{,}8622Z = -2{,}2155$

Plane 3 : The phenyl ring atoms (C(311), C(312), C(313), C(314), C(315), C(316))

$10{,}5265X + 0{,}0Y + 0{,}1770Z = 0{,}0443$

Plane 4 : The pyridine ring atoms (N(11), C(12), C(13), C(14), C(15), C(16))

$-0{,}3062X + 0{,}0Y + 16{,}1926Z = 4{,}0482$

Plane 5 : The pyridine ring atoms (N(41), C(42), C(43), C(44), C(45), C(46))

$-1{,}8912X + 22{,}1975Y - 2{,}7164Z = 3{,}2460$

Plane 6 : The phenyl ring atoms (C(111), C(112), C(113), C(114), C(115), C(116))

$5{,}9466X - 0{,}0034Y + 12{,}1103Z = 3{,}0284$

TABLE 3.7 CONT/....

(b) Deviations from the planes (Å x 10^3)

(σ x 10^3 < 20)

Atom	*Plane 1*
N(11)	-2178
C(111)	-6327
N(21)*	-1
C(22)*	-4
C(23)*	5
C(24)*	0
C(25)*	-5
C(26)*	6
C(27)	-46
C(311)	6102
N(41)	-218
Ni(1)	-101
N(31)	1973

Atom	*Plane 2*
N(11)	0
C(111)	0
N(21)	-1872
N(31)*	0
C(32)*	-1
C(33)*	1
C(34)*	0
C(35)*	-1
C(36)*	1
C(311)	0
N(41)	1872
Ni(1)	0

Atom	*Plane 3*
N(11)	0
C(111)	0
N(21)	-991
N(31)	0
C(311)*	0
C(312)*	-8
C(313)*	8
C(314)*	0
C(315)*	-8
C(316)*	8
N(41)	991
Ni(1)	0

Atom	*Plane 4*
N(11)*	0
C(12)*	-4
C(13)*	4
C(14)*	0
C(15)*	-4
C(16)*	4
C(111)	0
N(21)	1757
N(31)	0
C(311)	0
N(41)	-1757
Ni(1)	0

TABLE 3.7 CONT/....

Atom	*Plane 5*
N(11)	-2178
C(111)	-6327
N(21)	-218
N(31)	1973
C(311)	6102
N(41)*	-1
C(42)*	-4
C(43)*	5
C(44)*	0
C(45)*	-5
C(46)*	6
C(47)	-46
Ni(1)	-101

Atom	*Plane 6*
N(11)	-1
C(111)*	0
C(112)*	-8
C(113)*	8
C(114)*	0
C(115)*	-9
C(116)*	9
N(21)	721
N(31)	-2
C(311)	-2
N(41)	-723
Ni(1)	-1

(c) Angles between normals to planes (degrees)

Plane 1 and 2	85,4
Plane 1 and 3	78,2
Plane 1 and 4	79,2
Plane 1 and 5	30,5
Plane 1 and 6	75,0
Plane 2 and 3	33,6
Plane 2 and 4	116,6
Plane 2 and 5	94,6
Plane 2 and 6	81,0
Plane 3 and 4	83,0
Plane 3 and 5	101,8
Plane 3 and 6	47,4
Plane 4 and 5	100,9
Plane 4 and 6	35,6
Plane 5 and 6	105,1

TABLE 3.7 CONT/....

2 Selected torsion angles (degrees). The torsion angle $\omega(I\text{-}J\text{-}K\text{-}L)$ is defined as the angle between the vector $J\text{-}I$ and the vector $K\text{-}L$ when viewed down $J\text{-}K$. The sign of ω is positive if $J\text{-}I$ is to be rotated clockwise into $K\text{-}L$ and negative if anticlockwise[64].

C(13) - C(14) - C(111) - C(112)	-35,1
C(33) - C(34) - C(311) - C(316)	-33,2
N(11) - Ni(1) - N(21) - C(26)	-103,5
N(21) - Ni(1) - N(31) - C(36)	-118,8
C(32) - N(31) - Ni(1) - N(41)	61,2
C(42) - N(41) - Ni(1) - N(11)	73,2

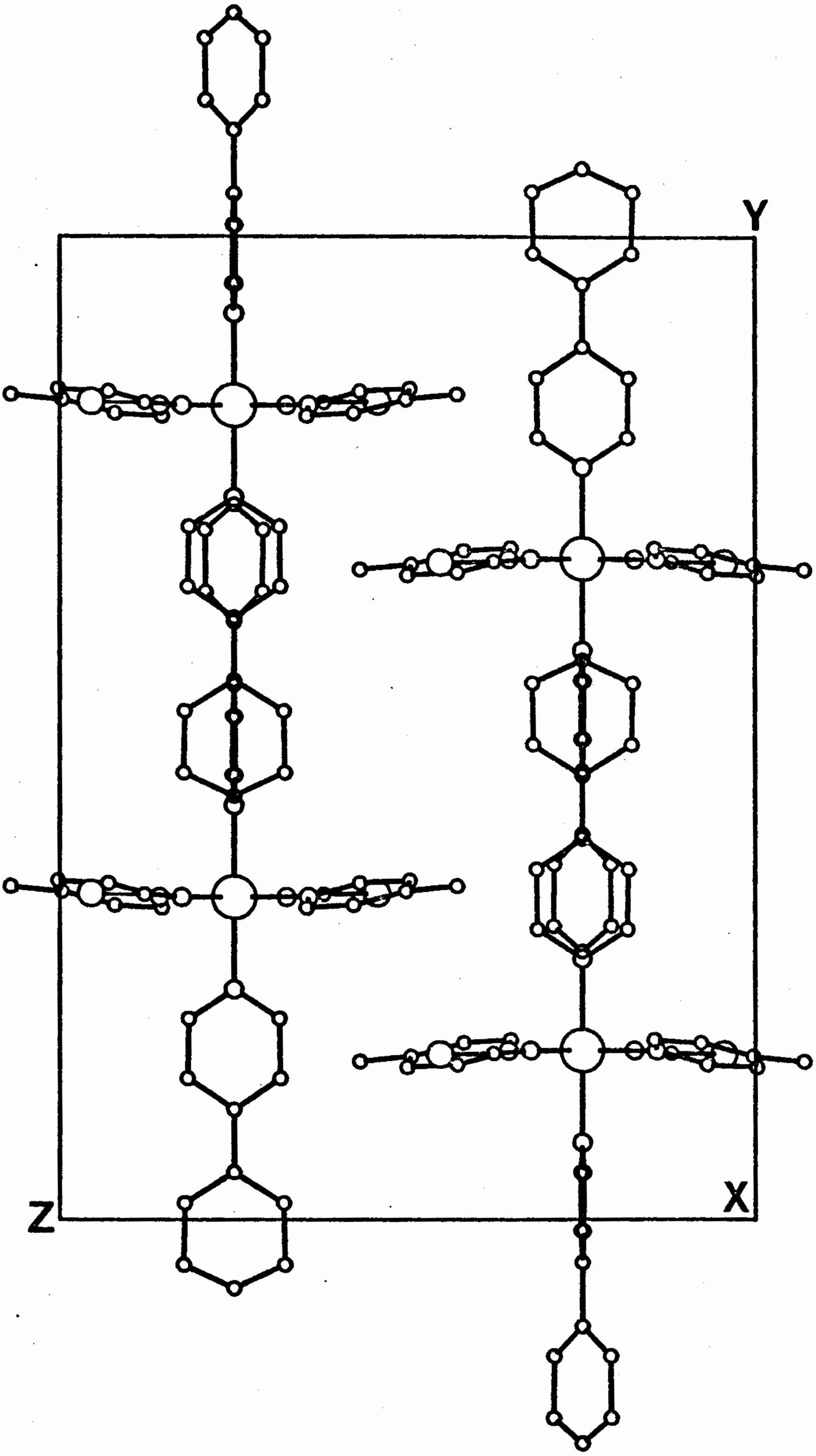


FIGURE 3.5 An illustration of the four host molecules in the unit cell.

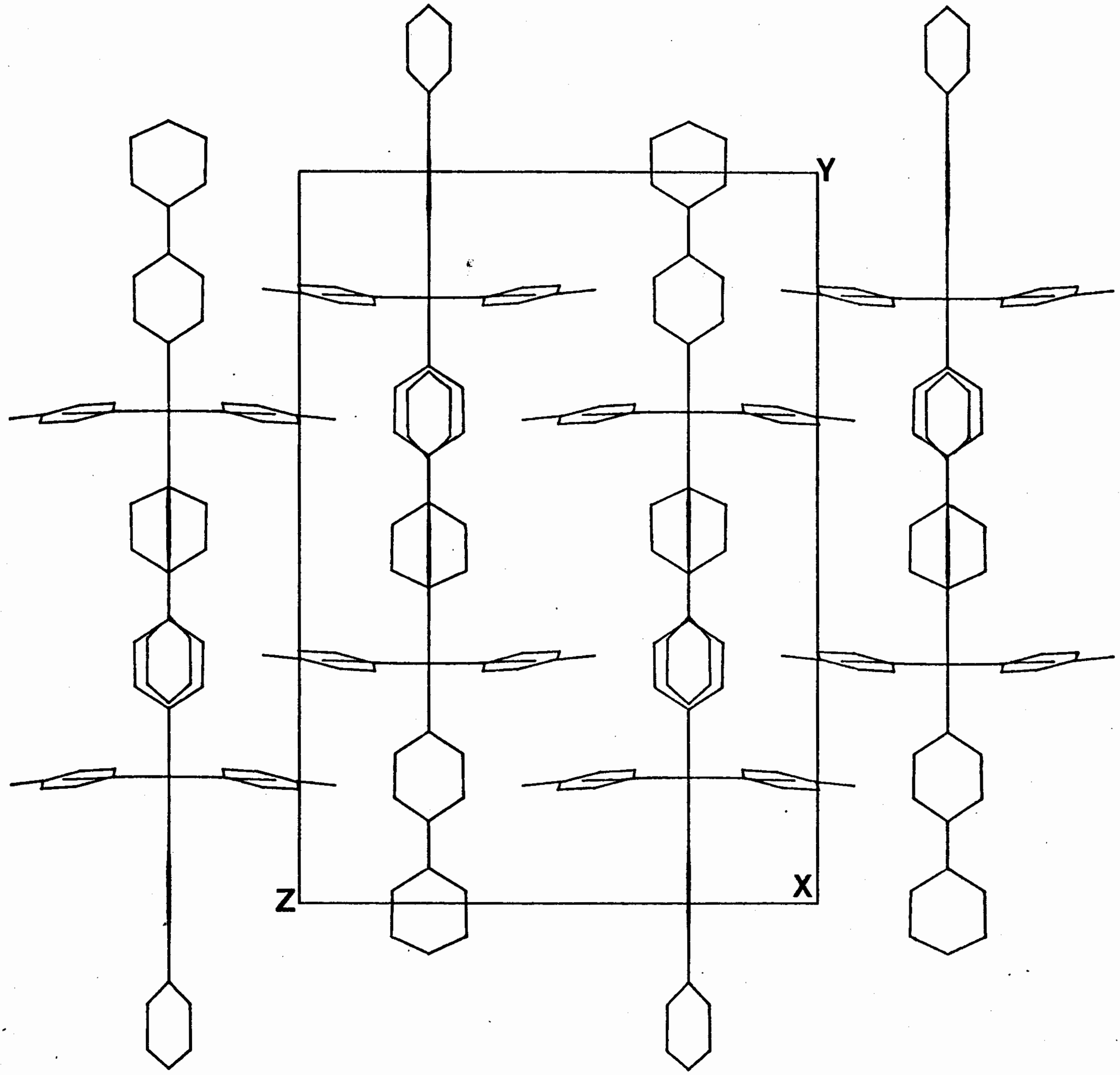


FIGURE 3.6 Packing of the host molecules in the unit cell shown in projection down the x axis.

and "tail" of 4-phenylpyridine with 4-methylpyridine "arms". The stack distance is ∿5Å. Furthermore, the host lattice surrounds a continuous channel of void space. The void space is divided into cavities by means of the isothiocyanate and pyridine ligand conformations. (A perspective view of the channel is shown in Figures 3.7 and 3.8.) Each cavity has a centre of inversion on which the non-centrosymmetric methyl cellosolve molecule is positioned. The molecule is inclined at an angle of $\sim 35^0$ with respect to the x axis, which is the direction of the channel. Disorder is invoked and in addition the methyl cellosolve molecules have considerable thermal motion. (Figure 3.9 illustrates the packing of the guest molecules in their cavities.)

The cavity dimensions are estimated to be 7,4 x 4,5 x 4,6Å. The methyl cellosolve molecule measured with van der Waal's radii has dimensions of 7,0 x 4,2 x 4,2Å. Thus the methyl cellosolve molecule is "snugly" enclosed within the host lattice.

Specific chemical guest-host interactions are absent. No shortening of intermolecular distances with respect to the sum of the van der Waal's radii are observed. Steric interactions alone appear responsible for holding the methyl cellosolve molecules captive in the host lattice.

Desorption of the guest molecules occurs readily from the relatively open channel structure. Kemula *et al*[49] propose that desorption is accompanied by variations in lattice parameters. These changes, although small, produce strains and the instability of the clathrate is visually observed. The crystals become non-transparent and brittle.

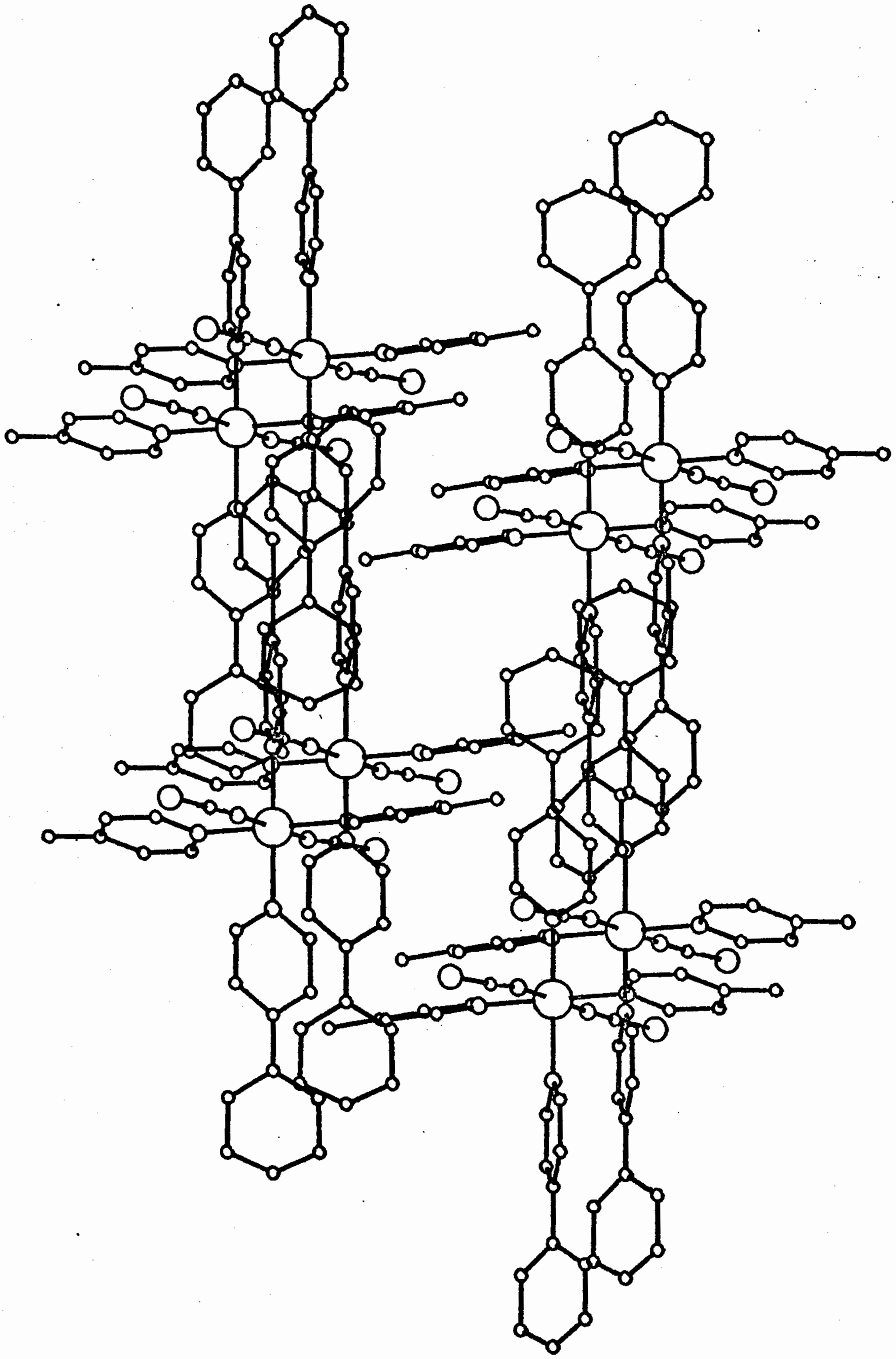


FIGURE 3.7 A perspective view of the channel.

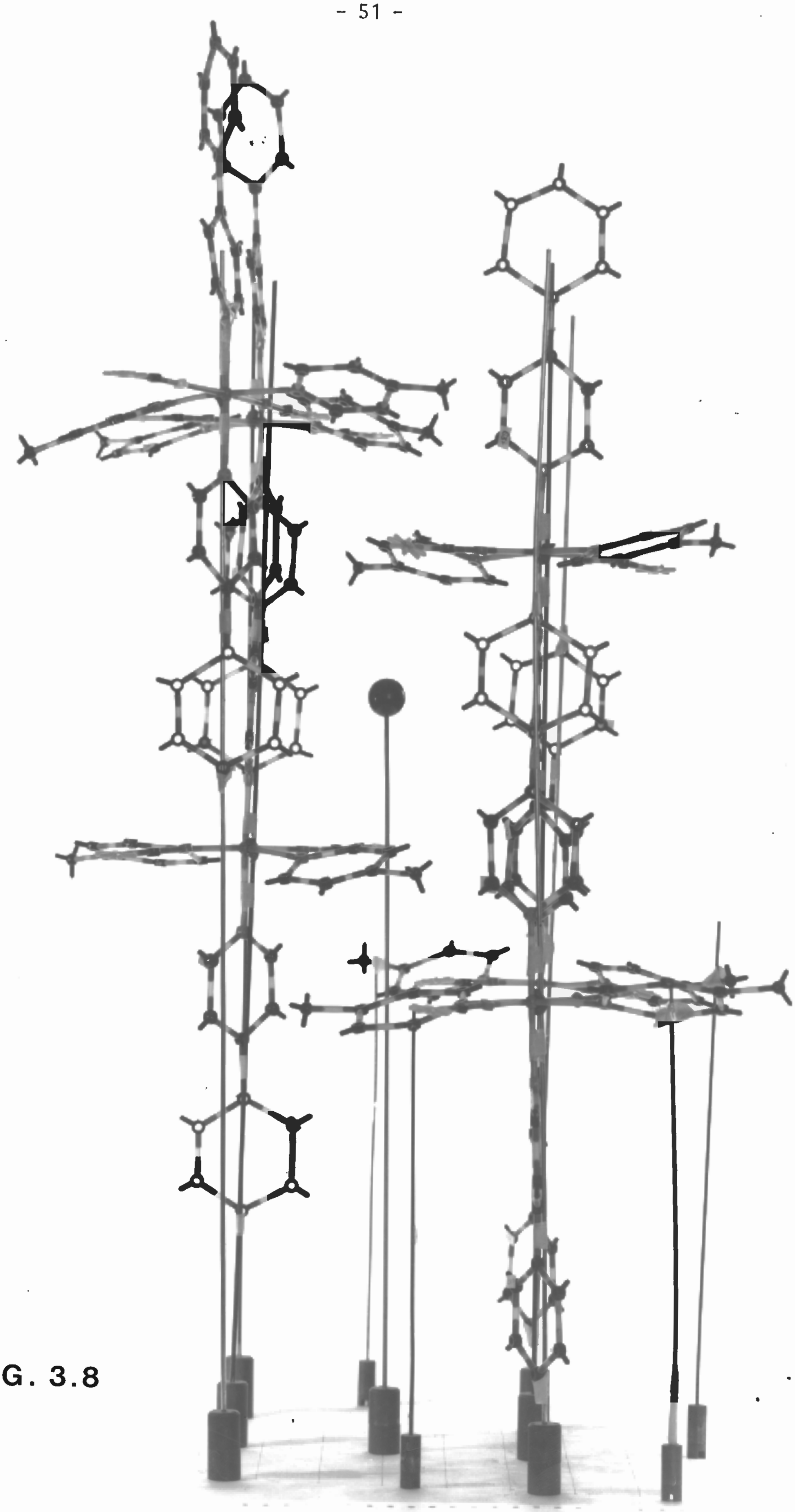


FIG. 3.8

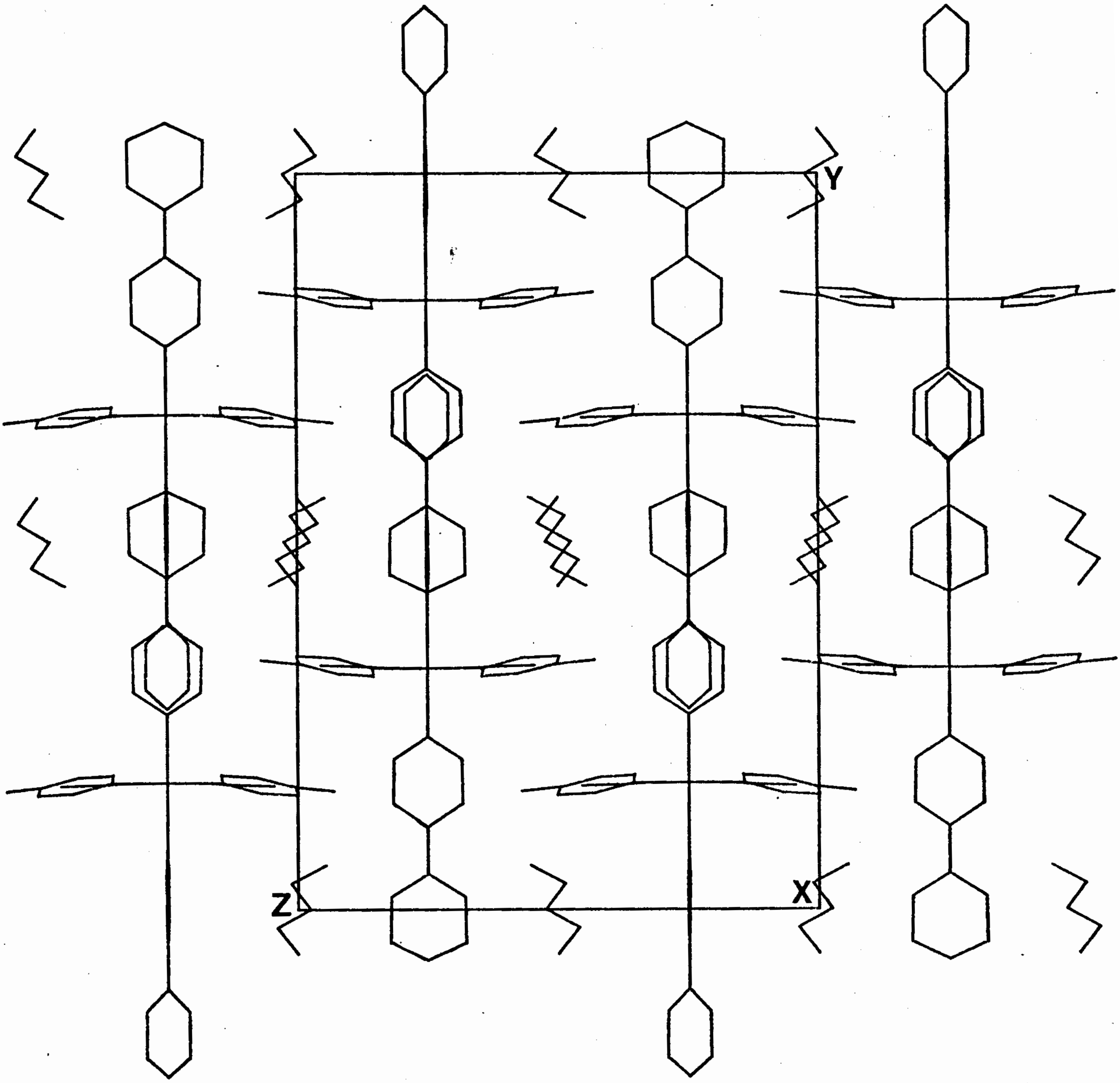


FIGURE 3.9 An illustration of the packing of the methyl cellosolve molecules in their cavities.

3.6 AN ENERGY STUDY OF THE METHYL CELLOSOLVE CLATHRATE

The potential energy environment of the methyl cellosolve molecule in the crystal lattice was studied in order to determine possible dynamic conformation changes in the host molecules and to ascertain the nature and strength of the forces holding the guest "captive" in the clathrate.

The program EENY[47] calculates the non-bonded potential energy of molecules using empirical atom-pair potential curves. The coefficients of the atom-atom potentials are of the form,

$$U(r) = a\exp(-br)/r^{d} - c/r^{6}$$

where r is the distance between any pair of atoms and coefficients a, b, c and d are those given by Giglio[52] such that $U(r)$ is evaluated in kilo=calories when r is in Ångström. The summation was extended over two unit cells and all atom-pairs found within this range were included in the calculation. However only an estimate of the non-bonded intermolecular interaction energy can be obtained from these potential energy calculations.

The input data for the geometry of the $Ni(NCS)_2(4\text{-}MePy)_2(4\text{-}PhPy)_2$ molecule were taken from the refined clathrate structure of this complex.

The study was divided into four parts.

Firstly, we evaluated the potential energy of the host-guest system with the guest molecule as located in the final refinement of the structure analysis. The symmetry conditions required that disorder be invoked to model the guest atoms. (This is detailed in Section 3.4) However, we arbitrarily chose one of the four possible orientations of the guest molecule. We calculated the positions of the methoxy and methylene hydrogens which are determined by the geometry of the molecule. The hydroxyl hydrogen was omitted because it has no fixed position. This guest molecule was then translated through the channel in steps of 1Å. The host lattice and the guest molecule were held rigid in these calculations.

Secondly, the same experiment was undertaken but after each translation of 1Å, the guest molecule was allowed small variations in its rotational parameters in order to find the local minimum in the energy profile.

Thirdly, the host lattice was allowed selected conformational freedom whereas the methyl cellosolve molecule was rigidly held at various lattice sites.

Finally, the model was extended to encompass both conformational freedom of the host and rotational freedom of the guest.

Energy Run 1

Figure 3.10 illustrates the two unit cells with host molecules defined by the notation (n, t_x, t_y, t_z) where n is the symmetry operator and t_x, t_y and t_z the unit cell translations. In addition, the ten translatory sites of the methyl cellosolve molecule are indicated for clarity. The non-bonded interaction between the methyl cellosolve molecule positioned at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ and the host lattice was calculated. "Close contacts" between the guest molecule and the 3000 and 4000 host molecules arise. Furthermore, the energy sum is low, -4,1kcal, indicative of favourable guest-host interaction. The methyl cellosolve molecule was translated 1Å in the x direction *i.e.* along the channel. The energy increased to 8,9kcal. The energy sum calculated at successive translatory sites along the channel is clearly depicted by Graph 1 in Figure 3.11.

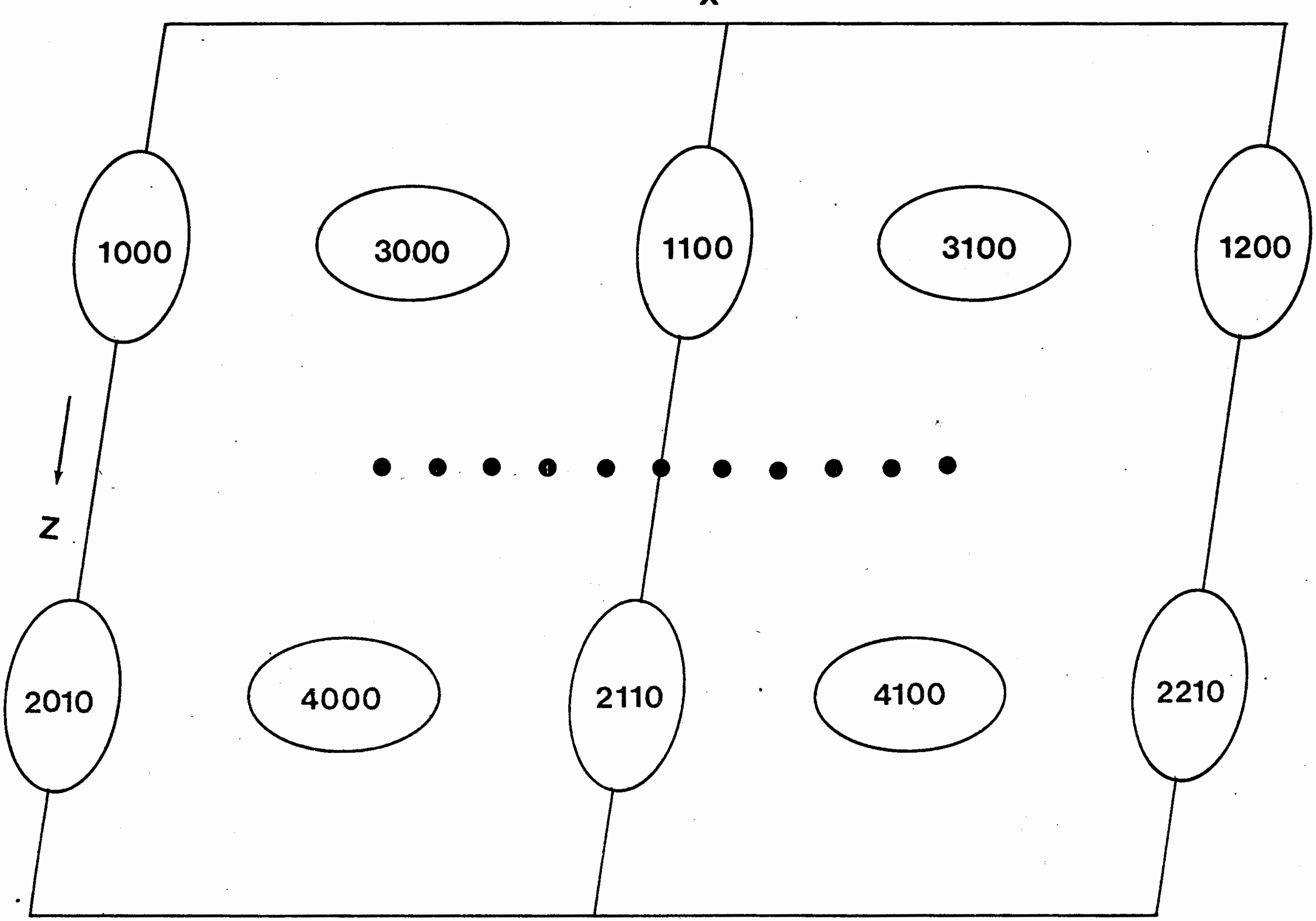


FIGURE 3.10 Translatory positions of the methyl cellosolve molecule are indicated by ●.

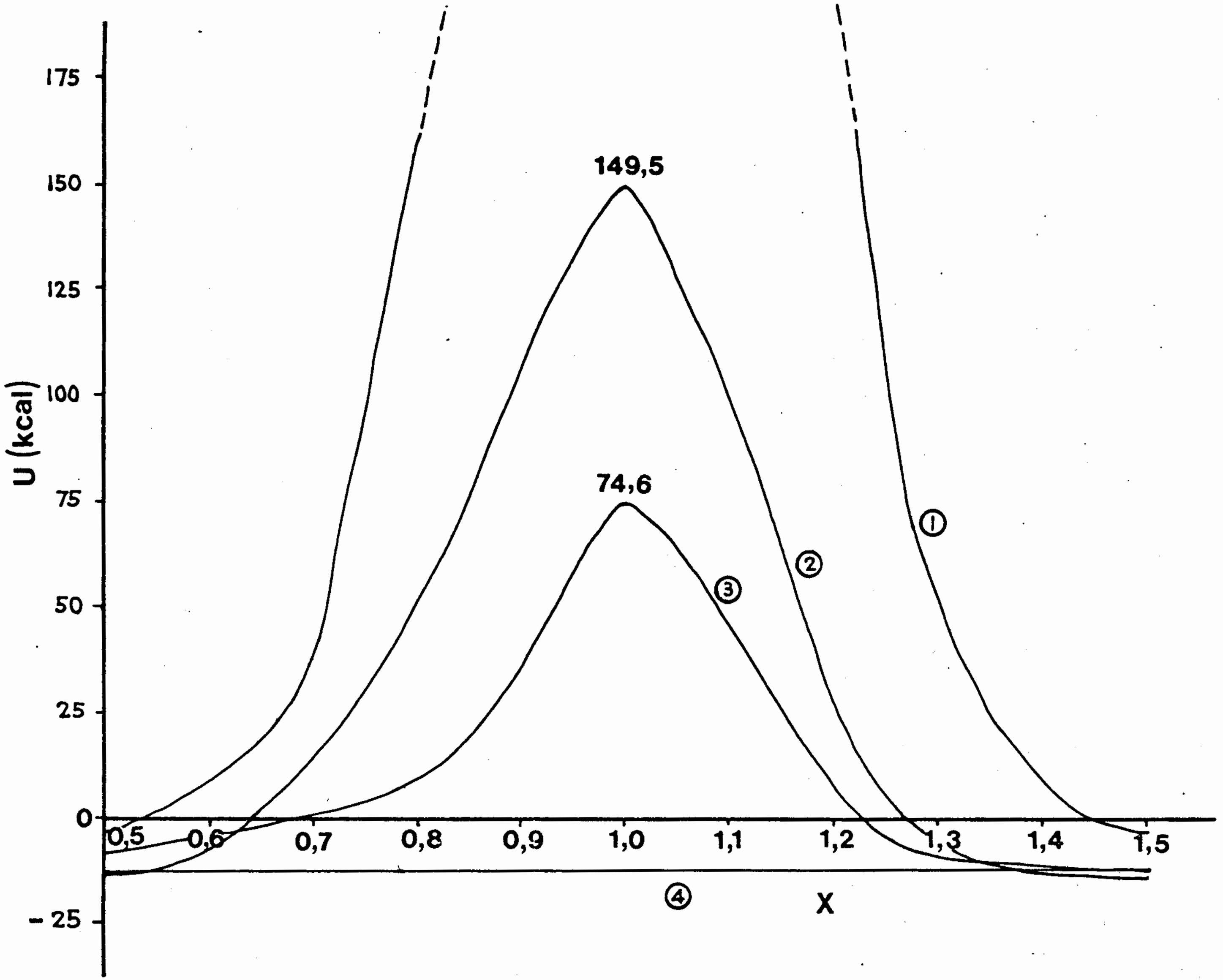


FIGURE 3.11 A plot of (non-bonded) potential energy (*U*) versus guest translatory positions.

With this energy model, we see that the guest is effectively trapped at the $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ site and any translational movement along the channel immediately gives rise to repulsion by the host molecules.

Energy Run 2

The above model was refined by allowing the methyl cellosolve molecule small variation in its rotational parameters in order to find a local minimum in the energy profile after every 1Å translation. The result of this mode of translation of the guest molecule is illustrated by Graph 2 in Figure 3.11.

Furthermore the non-bonded intermolecular energy between the guest molecule at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ and the host molecules is reduced to -13,55kcal. This would imply that the guest molecule requires rotational freedom in order to orientate itself most favourably with respect to the host molecules and in so doing minimise repulsive interaction. In addition a less rigid guest molecule will negotiate the more exacting apertures along the channel far better, hence the lowering of the energy barrier.

Energy Run 3

In this model, the host lattice was allowed selected conformational freedom whereas the guest molecules were held rigid at the various translatory sites.

The host molecule was systematically divided into seven residues linked by six torsion angles as follows;

τ_1 [N(1) - Ni - N(41) - C(46)]

τ_2 [N(2) - Ni - N(21) - C(26)]

τ_3 [N(1) - Ni - N(31) - C(32)]

τ_4 [C(33) - C(34) - C(311) - C(312)]

τ_5 [N(2) - Ni - N(11) - C(12)]

τ_6 [C(13) - C(14) - C(111) - C(112)]

(Refer to Figure 3.12)

The conformation of the pyridine ligands was determined from the torsion angle values calculated from the input data. The intramolecular energy for the rigid host molecule with $\tau_1 = \tau_2 = -13{,}66$, $\tau_3 = -28{,}98$, $\tau_4 = 146{,}81$, $\tau_5 = -34{,}22$ and $\tau_6 = -35{,}05^{\circ}$ was calculated to be 3,12kcal. By considering the values obtained for τ_1, τ_2, τ_3 and τ_5 we propose that the centrosymmetric host molecule belongs to the (----) or the enantiomeric (++++) conformational type[53]. (Correlation of host structure to conformational type is detailed in Section 4.6.)

The six residues 2, 3, 4, 5, 6 and 7 (See Figure 3.12) were then allowed freedom of rotation in order to minimise repulsive interaction with the rigid guest molecule as it translated through the channel. The result is represented in Figure 3.11 by graph 3. The energy barrier is further reduced to 75kcal.

Energy Run 4

Finally, the model was adapted to allow both host conformational and guest rotational freedom. An energy barrier is not observed. (See Graph 4 in Figure 3.11.) In fact, at each translatory site the guest molecule has an equally favourable orientation with respect to the host molecules. The guest is no longer restricted to the site at ½, ½, ½ but may freely diffuse through the channel.

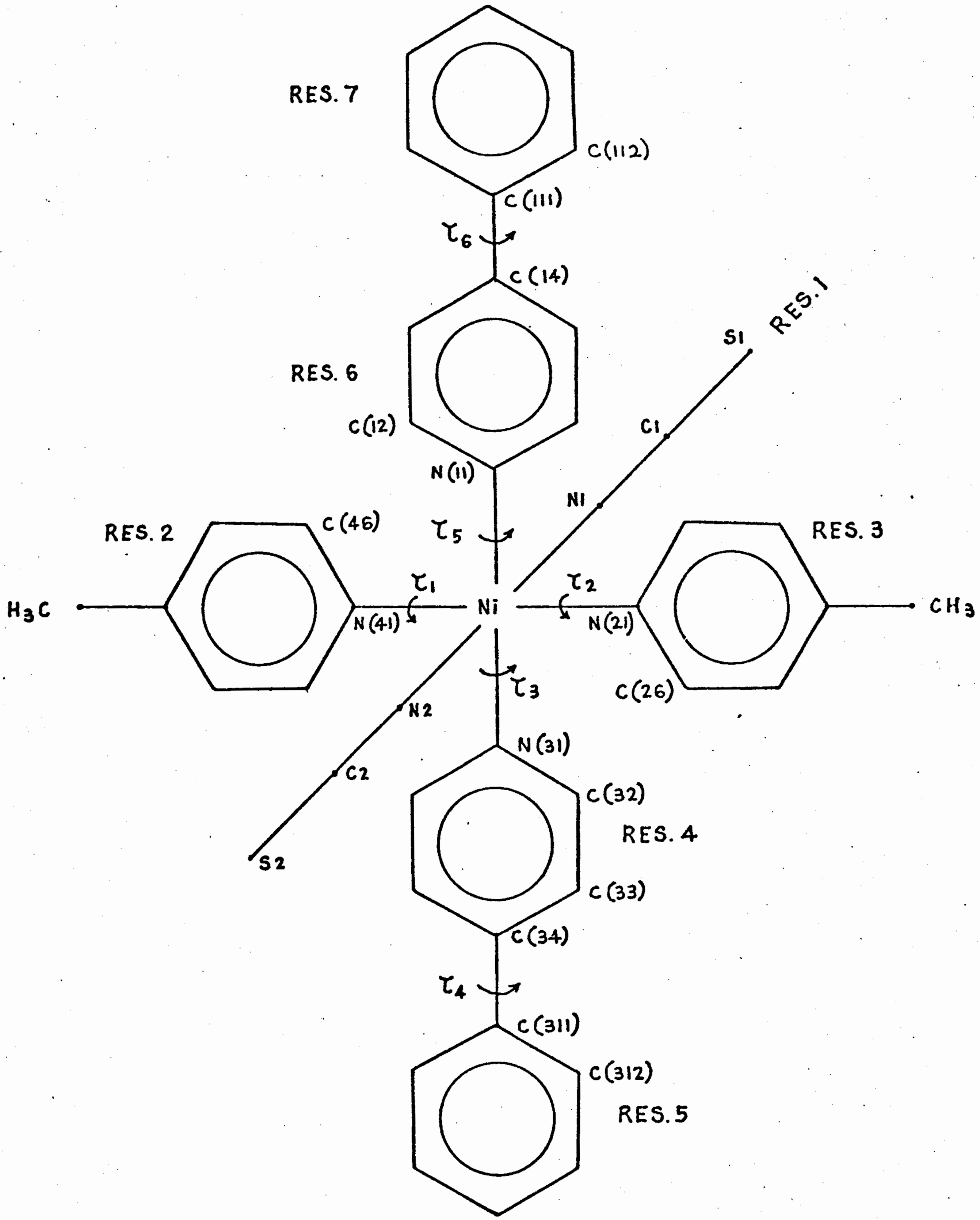


FIGURE 3.12 The host molecule sub-divided into 7 residues linked by 6 torsion angles.

We suggest that a realistic clathrate energy model should include a guest with rotational freedom and a host lattice with restricted conformational freedom of the pyridine and isothiocyanate ligands.

We predict that in the enclathration process, the host molecules adopt a specific conformation in order to trap the guest molecules and in so doing prevent their free translation along the channel.

CHAPTER 4

CHAPTER 4

THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(ISOTHIOCYANATO)TETRA(4-METHYL=PYRIDINE)NICKEL(II).P-CYMENE (CYMEN)

4.1 EXPERIMENTAL AND CHARACTERISATION

Synthesis

The host complex, $Ni(NCS)_2(4\text{-}MePy)_4$ was prepared as in Section 3.1. (Found: 57,10%C, 5,10%H and 15,30%N, Calculated: 57,05%C, 5,16%H and 15,35%N).

Clathrate preparation by Schaeffer's solution method[48] produced crystals of microscopic dimensions unsuitable for crystallographic use. Instead relatively large crystals were obtained by the following method: 0,06g (0,00011mole) of dry Werner complex was dissolved in 5ml of chloroform. 0,7ml (0,00046mole) of the guest, p-cymene, was added to the above dark blue solution. Crystallisation of the $Ni(NCS)_2(4\text{-}MePy)_4$. p-cymene clathrate occurred overnight at room temperature. Distorted hexagonal-shape crystals were kept immersed in mother liquor (chloroform and p-cymene) to prevent deterioration in air.

Analyses

Mass Spectroscopy

The presence of p-cymene in the clathrate was confirmed by mass spectroscopy. The mass spectrum (in tabulated form) with proposed fragmentational assign=ment is shown in Table 4.1.

TABLE 4.1 MASS SPECTRUM FOR CYMEN

m/e	Relative % Abundance	Possible Inference
Table A (Guest & Host)		
28	27	N_2^+
39	20	$C_3H_3^+$
51	10	$C_4H_3^+$
65	24	$C_5H_5^+/C_4H_3N^+$
66	36	$C_4H_4N^+$
78	5	$C_5H_4N^+$
91	15	$C_7H_7^+$
92	24	$C_6H_6N^+$
93	100	$C_6H_7N^+$
119	90	$C_9H_{11}^+$
134	26	$C_{10}H_{14}^{+\cdot}$
Table B (Host)		
28	22	N_2^+
39	17	$C_3H_3^+$
51	7	$C_4H_3^+$
65	21	$C_5H_5^+/C_4H_3N^+$
66	39	$C_4H_4N^+$
78	4	$C_5H_4N^+$
92	27	$C_6H_6N^+$
93	100	$C_6H_7N^+$

It was evident that the stability of this clathrate, CYMEN, differed from that of the previous clathrate, PYRID. Preferential volatilisation and ionisation of guest followed by host breakdown was not observed.

The fragmentation pattern obtained at low scan numbers of the total ion current (*Table A*) could not be related to the structure of p-cymene alone. p-Cymene was unambiguously identified by the presence of the m/e = 134, 119 and 91 peaks in particular. However, the relative abundance of the m/e = 93 peak was far greater than is recorded for the spectrum of p-cymene under similar experimental conditions. In addition, the m/e = 66 fragment assigned $C_4H_4N^+$ with a 36% relative abundance cannot possibly be related to p-cymene ($C_{10}H_{14}$). It was concluded that simultaneous breakdown of p-cymene and the host complex occurred at the lower scan numbers.

The fragmentation pattern obtained at higher scan numbers (*Table B*) was related to the host structure alone.

Thermogravimetric Analysis and Differential Thermal Analysis

Thermoanalytical investigations of clathrates provide information as to their physico-chemical properties. The simultaneous use of Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) allowed meaningful interpretation of the thermal decomposition reactions. (DTA measures the change in heat content as a function of increasing tempera= ture whereas TGA is a measure of weight change as a function of increasing temperature.)

The measurements were made on the Stanton-Redcroft model TR thermobalance. A quartz tube contained the 120,8mg sample of clathrate crystals. The sample was heated to 550°C at a rate of 6°C/min. The chart speed was 300mm/hour.

The thermal decompostion of the $Ni(NCS)_2(4\text{-}MePy)_4$.p-cymene clathrate is presented graphically in Figure 4.1.

Thermal decomposition begins only once the host lattice has been destroyed, *i.e.* the escape of the guest, p-cymene, occurs simultaneously with the evaporation of the first of the four 4-methylpyridine ligands of the host complex. Lewartowska *et al*[54] and Kemula *et al*[49] confirm this observation.

Four distinct thermal decomposition reactions are observed. An initial weight loss between 160°C and 200°C is a result of the simultaneous evaporation of p-cymene and a 4-methylpyridine ligand. A further loss of two 4-methylpyridine ligands occurs in the range 200 to 226°C. After 230°C the TGA curve is complex consisting of various small inflections which makes unambiguous assignment difficult. The DTA curve however clearly illustrates two decomposition reactions occurring between 300 and 350°C. Breakdown of the remaining 4-methylpyridine ligand (300 - 320°C) is directly followed by decomposition of one isothiocyanate group (320 - 350°C). Finally, gradual loss of weight between 350°C and 550°C may be due to the second "sluggish" isothiocyanate group decomposition. After 550°C only nickel remains and constant weight is attained.

A quantitative estimate of the guest content based on the above assign=ments was made. The guest to host molar ratio was thus determined as 0,77 : 1.

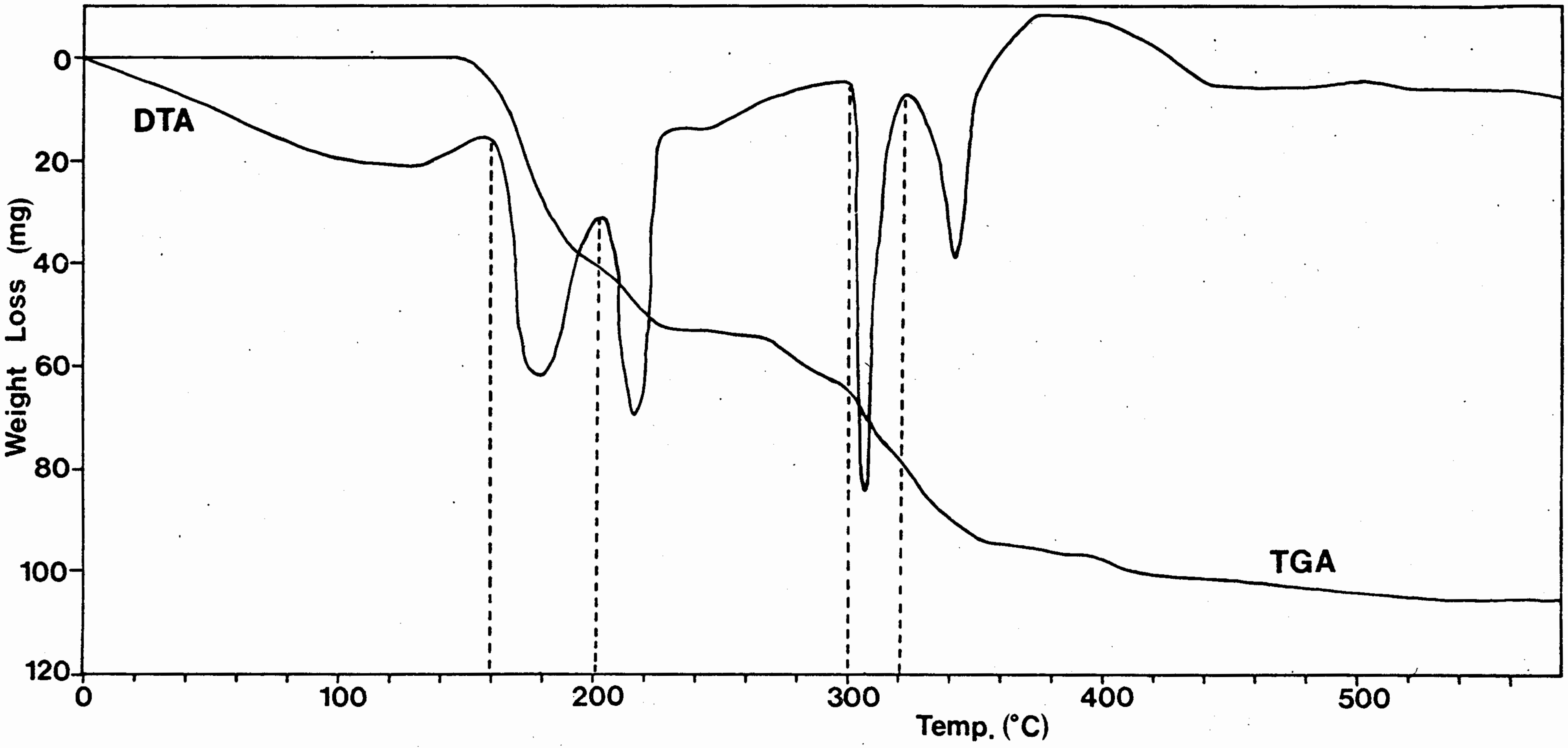


FIGURE 4.1 The TGA and DTA thermal decomposition curves of the p-cymene clathrate.

Quantitative Proton Nuclear Magnetic Resonance Spectroscopy

The ^1H N.M.R. spectrum of the $Ni(NCS)_2(4\text{-}MePy)_4$.p-cymene clathrate is shown in Figure 4.2.

The paramagnetic nature of the Ni^{2+} ion causes considerable shifting of the 4-methylpyridine ligand resonances from their normal resonance positions. In addition, individual mehtyl and aromatic signals cannot be distinguished. The 4-methylpyridine ligands are therefore responsible for the large, broad singlet at -7,52δ which integrates for twenty-eight hydrogens.

The remaining signals are produced by the guest, p-cymene. The integration distributes the fourteen hydrogens thus; six hydrogens to the doublet centred at δ1,24, three hydrogens to the singlet at 2,30, one hydrogen to the small, broad peak at 2,89 and four hydrogens to the singlet at 7,09.

Comparison of the amount of integration for the p-cymene protons with that of the 4-methylpyridine protons allowed an estimation of the guest to host molar ratio. The ratio was determined as 0,66 : 1.

Density Determination

The density of the crystal was determined as 1,24gcm^{-3} by flotation in a mixture of saturated potassium iodide and water. The number of molecules per unit cell approximated eight when assuming a 1 : 1 guest to host molar ratio. (Crystal structure analysis confirmed the Z_H value as 8.)

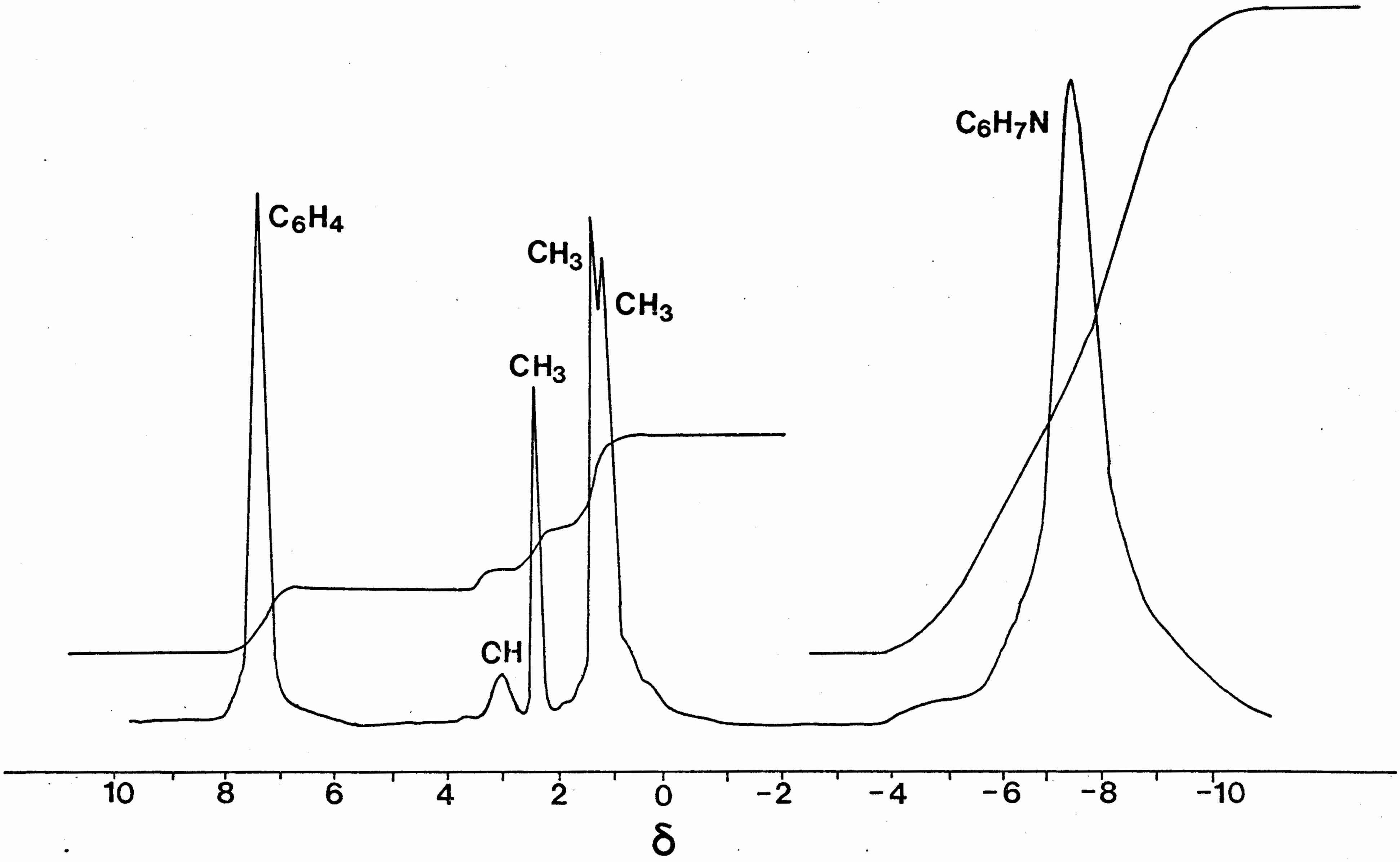


FIGURE 4.2 The ^{1}H N.M.R. spectrum of the p-cymene clathrate.

A quantitative estimate of the guest to host molar ratio was obtained from the density measurement (D_m).

Once again employing the equation,

$$Z_H(M_H) + Z_G(M_G) = ND_m abc\sin\beta \times 10^{-24}$$

where,

$Z_H = 8$: Number of host molecules per unit cell
$M_H = 547{,}382$: Molecular weight of host in gmol^{-1}
$M_G = 134{,}21$: Molecular weight of guest in gmol^{-1}
$N = 6{,}023 \times 10^{23}$: Avogadro constant
$D_m = 1{,}24(\pm 0{,}01)$: Measured density in gcm^{-3}
$abc\sin\beta = 6973{,}85(\pm 6{,}26)$: Volume of unit cell in $\mathrm{Å}^3$

Z_G, the number of guest molecules per unit cell, was calculated to be 6,18(±0,05). The guest to host molar ratio is thus 0,77(±0,01) : 1.

Analytical Determination of Nickel Content

In order to calculate the guest to host molar ratio, it was necessary to determine the stoicheiometric amount of p-cymene present in the clathrate.

A 0,03 - 0,05g sample of clathrate crystals was dissolved in 10ml of 0,5M HCl. This solution was analysed for Ni^{2+} by complexiometric titration with 0,1M EDTA in ammoniacal solution against murexide as indicator. The amount of guest was read from the difference between the weight of the clathrate sample and the weight of host as determined above.

Results	Experiment 1	2	3
Weight of sample in g	0,0340	0,0440	0,0335
Titre of EDTA in ml	5,42	7.07	5,40
Weight of p-cymene in g	0,0043	0,0053	0,0039
Guest to host molar ratio	0,6 : 1	0,56 : 1	0,54 : 1

Although consistent results were not obtained, further experimentation was not possible due to the lack of clathrate sample. (All analyses were determined on the same batch of clathrate crystals.)

The following experimental errors may account for the discrepancy in the guest to host molar ratio values.

(1) Neglecting to allow the sample to digest in HCl for the same necessary length of time, *i.e.* incomplete digestion.

(2) Difficulty was encountered in the visual detection of the endpoint.

(3) The complexation of Ni^{2+} with murexide is a "sluggish" process. The endpoint may thus be easily overshot.

We conclude that the guest to host molar ratio values obtained by these various techniques conform reasonably well. In addition, the time lapse between the analyses could be responsible for the discrepancies. (Guest desorption does occur with time.) The density determination and the thermogravimetric run were promptly carried out employing the fresh crystals, hence an explanation for their higher guest to host molar ratio values.

The guest to host molar ratio is thus assumed as 0,77 : 1.

4.2 PRELIMINARY X-RAY ANALYSIS

The symmetry displayed by the oscillation and Weissenberg photographs indicated a tetragonal space group.

The cell parameters estimated from the photographs were as follows; a = 17,10Å, b = 17,10Å, c = 23,72Å, $\alpha = \beta = \gamma = 90^{\circ}$ and $Z = 8$.

The conditions for non-extinction of reflections evident from the zero and upper layer Weissenberg photographs were;

hkl : $h + k + l = 2n$
$hk0$: $h, (k) = 2n$
$00l$: $l = 4n$

These conditions limiting the hkl, $hk0$ and $00l$ reflections uniquely defined the space group as $I4_1/a$[50].

4.3 INTENSITY DATA COLLECTION

4157 reflections collected within the range $6^{\circ} < 2\theta < 54^{\circ}$ constituted the diffractometer data set. 285 were excluded as systematically absent and a further 1616 were suppressed as they did not satisfy the criterion $I_{rel} > 2\sigma I_{rel}$. The "observed" data therefore contained 2024 reflections. After every 55 reflections, three reference reflections were measured and were found to remain constant to within 0,68% of their mean value. The diffractometer scan width was 1,30°θ and the scan speed, $0{,}043^{\circ}\theta s^{-1}$.

Accurate cell parameters, determined by least squares analysis, are listed in Table 4.2.

TABLE 4.2 CRYSTAL DATA

Molecular formula	$C_{34}H_{39}N_6NiS_2$
Molecular weight	654,558gmol^{-1}
Space group	$I4_1/a$
a	17,105(9)Å
b	17,105(9)Å
c	23,837(12)Å
$\alpha = \beta = \gamma$	90°
V	6973,85Å^3
D_m	1,24gcm^{-3}
D_c	1,24gcm^{-3}
$\mu(\mathrm{MoK}_\alpha)$	6,58mm^{-1}
$F(000)$	2865
Crystal dimensions	0,63 x 1,00 x 0,75mm
Scan mode	ω-2θ
Scan width	1,30°θ
Scan speed	0,043°θs^{-1}

4.4 SOLUTION AND REFINEMENT OF THE CLATHRATE STRUCTURE

4.4.1 THE HOST COMPLEX, $Ni(NCS)_2(4\text{-}MePy)_4$

A three-dimensional Patterson map was computed in order to locate the position of the nickel atom. The $I4_1/a$ space group has sixteen general positions available for molecular occupation. However, with only eight molecules per unit cell, the nickel atoms must lie at the special positions, denoted by Wyckoff as *e* or *d*. Appropriate vector grids were constructed and the unique vector types derived are as follows;

Wyckoff Position *e*	Vector Position	Multiplicity
	0, 0, 0	4
	0, 0, $2z$	2
	0, 0, $-2z$	2
	0, $\frac{1}{2}$, $\frac{1}{4}$	2
	0, $\frac{1}{2}$, $\frac{3}{4}$	2
	0, $\frac{1}{2}$, $\frac{1}{4} + 2z$	1
	0, $\frac{1}{2}$, $\frac{1}{4} - 2z$	1
	0, $\frac{1}{2}$, $\frac{3}{4} + 2z$	1
	0, $\frac{1}{2}$, $\frac{3}{4} - 2z$	1

Wyckoff Position *d*	Vector Position	Multiplicity
	0, 0, 0	4
	0, $\frac{1}{2}$, 0	2
	$\frac{1}{2}$, 0, 0	2
	$\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$	1
	$\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$	1
	$\frac{1}{4}$, $\frac{3}{4}$, $\frac{1}{4}$	1
	$\frac{3}{4}$, $\frac{1}{4}$, $\frac{3}{4}$	1

$\frac{1}{4}, \frac{1}{4}, \frac{3}{4}$	1
$\frac{3}{4}, \frac{3}{4}, \frac{1}{4}$	1
$\frac{1}{4}, \frac{3}{4}, \frac{3}{4}$	1
$\frac{3}{4}, \frac{1}{4}, \frac{1}{4}$	1

The nickel atom was located at the 0, 0, $2z$ vector position, which is derived from the vector grid for the special positions denoted by Wyckoff as *e*. (The host molecules therefore have two-fold axial symmetry.) The z coordinate of the nickel atom was established as 0,178 and the x and y coordinates were fixed at 0.

A weighted electron density difference map phased on the nickel atom revealed two atoms in close proximity to the metal at distances of approximately 2,0Å. These three atoms and the anisotropic temperature factors calculated for the nickel atom[51] were included in the subsequent electron density calculation. The positions of fourteen more non-hydrogen atoms were revealed with the residual R factor equal to 0,44. The remaining non-hydrogen atom as well as four guest atoms were located in the following difference fourier thereby substantially reducing R to 0,17.

The host molecule has two-fold axial symmetry, hence the necessity to locate the atomic positions of the asymmetric unit only.

4.4.2 LOCATION OF THE GUEST, p-CYMENE ($C_{10}H_{14}$)

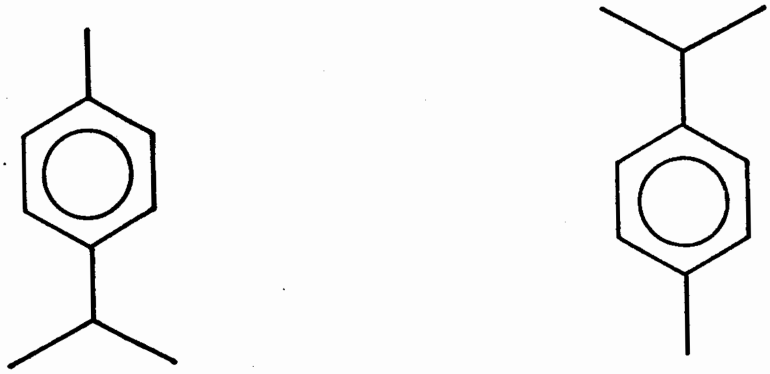
A further four cycles of least squares refinement did not reveal the position of the remaining guest atoms.

A difference fourier phased on the host non-hydrogen atoms only, was computed and electron density maps obtained at intervals of y = 0,03.

A region of high electron density was located between the two-dimensional slices y = 0,06 and y = -0,06. The three-dimensional electron density map, contoured at intervals of 0,2eÅ^{-3} is illustrated in Figure 4.3.

The carbon atoms of the aromatic p-cymene ring were easily pin-pointed and their coordinates estimated. However considerable difficulty was encountered in locating the positions of the substituent methyl- and isopropyl- groups of the p-cymene molecule. The guest molecule lies on a centre of inversion at 0,25, 0, 0,375. Statistical disorder was invoked because the p-cymene molecule is not centrosymmetric. The p-cymene molecule thus has two equally probable orientations as shown in Figure 4.4.

FIGURE 4.4


(a) (Head-Tail conformation) (b) (Tail-Head conformation)

These combine to give

(c)

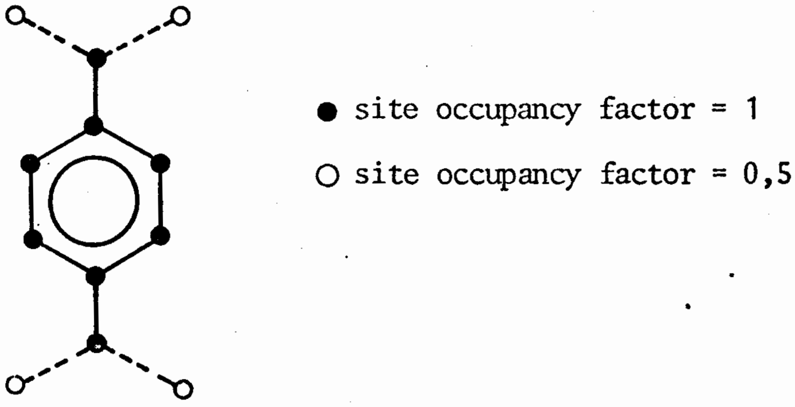
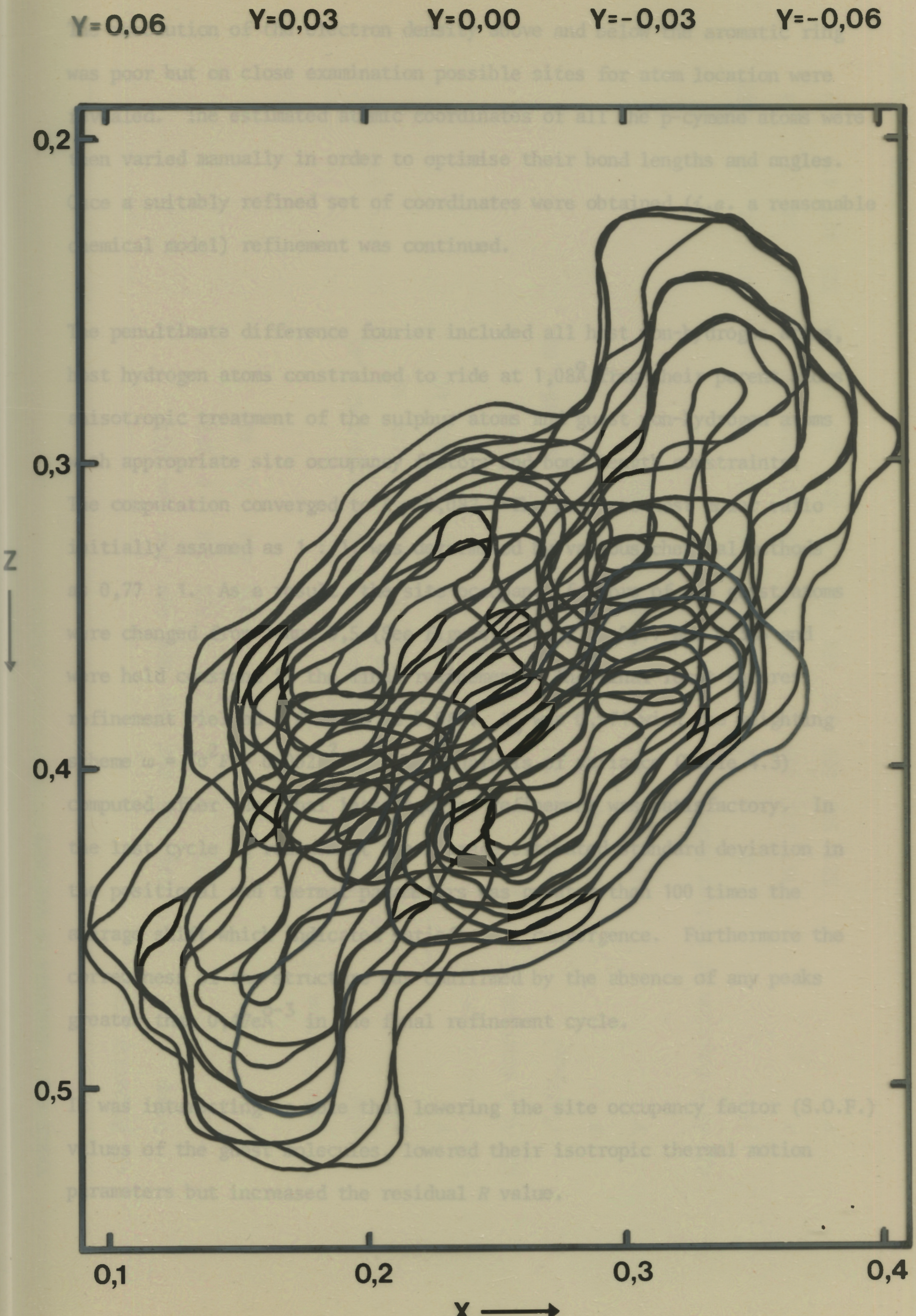


FIGURE 4.3 A three-dimensional electron density map.


Y=0,06
Y=0,03
Y=0,00
Y=-0,03
Y=-0,06
0,2
0,3
0,4
0,5
Z
0,1
0,2
0,3
0,4
X

The resolution of the electron density above and below the aromatic ring was poor but on close examination possible sites for atom location were revealed. The estimated atomic coordinates of all the p-cymene atoms were then varied manually in order to optimise their bond lengths and angles. Once a suitably refined set of coordinates were obtained (*i.e.* a reasonable chemical model) refinement was continued.

The penultimate difference fourier included all host non-hydrogen atoms, host hydrogen atoms constrained to ride at 1,08Å from their parent atoms, anisotropic treatment of the sulphur atoms and guest non-hydrogen atoms with appropriate site occupancy factors and bond length constraints. The computation converged to $R = 0{,}087$. The guest to host molar ratio initially assumed as 1 : 1, was determined by various chemical methods as 0,77 : 1. As a result, the site occupancy factors of the guest atoms were changed from 1 and 0,5 (See Figure 4.4(c)) to 0,77 and 0,385 and were held constant in the final refinement. The final least squares refinement yielded a R value of 0,089. R_ω was 0,971 with the weighting scheme $\omega = (\sigma^2 F + 0{,}002F^2)^{-1}$. The analysis of variance (Table 4.3) computed after the final least squares refinement was satisfactory. In the last cycle of refinement the average estimated standard deviation in the positional and thermal parameters was greater than 100 times the average shift which indicated satisfactory convergence. Furthermore the correctness of the structure was confirmed by the absence of any peaks greater than 0,47eÅ^{-3} in the final refinement cycle.

It was interesting to note that lowering the site occupancy factor (S.O.F.) values of the guest molecules, lowered their isotropic thermal motion parameters but increased the residual R value.

TABLE 4.3 ANALYSIS OF VARIANCE

---

a) By parity groups

Group	*ggg*	*ugg*	*gug*	*uug*	*ggu*	*ugu*	*guu*	*uuu*	All
N	515	0	0	453	0	528	528	0	2024
V	514	0	0	493	0	479	481	0	491

b) As a function of sinθ

sinθ 0,00-0,18-0,23-0,26-0,29-0,32-0,34-0,37-0,39-0,42-0,46

N	213	222	187	202	240	151	262	174	219	154
V	864	602	465	414	422	380	356	320	340	467

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

$\surd(F/F_{max})$ 0,00-0,21-0,22-0,24-0,26-0,28-0,30-0,34-0,39-0,48-1,00

N	320	148	238	187	185	145	202	199	204	196
V	456	455	486	523	447	431	528	497	580	485

d) As a function of |Miller index|

$\|h\|$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	157	275	283	244	223	179	158	139	108	87	72	45	38	12	4
V	521	500	609	575	488	489	430	381	342	366	334	329	407	411	479

TABLE 4.3 CONT/....

TABLE 4.3 CONTINUED

$\lvert k \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	7	21	41	58	83	105	118	126	150	150	157	153	160	150	545
V	770	528	754	748	751	662	598	569	543	451	434	395	341	391	378

$\lvert l \rvert$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	REST
N	82	103	118	148	97	123	107	87	118	118	70	122	78	61	592
V	451	594	685	500	687	544	442	542	419	443	626	406	426	470	402

N = No. of reflections in the group

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

The *R*-factor ratio (*ℛ*) test[55] was employed in order to decide whether a significant worsening of the agreement between observed and calculated structure factors had occurred. A Null hypothesis proposed that there was a significant difference in the correctness of the structure on lowering the S.O.F. values. However, the *R*-factor ratio (*ℛ*) calculated at significant levels of 0,05, 0,10 and 0,50 lies well within the rejection area at each significant level. It was concluded that no significant difference in the correctness of the structure had occurred even though the residual *R* value had increased.

The final coordinates with corresponding thermal motion parameters are listed in Table 4.4. Observed and calculated structure factors are shown in Appendix 2.

4.5 DESCRIPTION OF THE CLATHRATE STRUCTURE

4.5.1 MOLECULAR STRUCTURE

A perspective view of the host complex with atomic nomenclature for the asymmetric unit is shown in Figure 4.5. Intramolecular bond lengths and angles with estimated standard deviations are listed in Tables 4.5 and 4.6 respectively.

The centrosymmetric host molecule adopts two-fold axial symmetry. The nickel atoms is octahedrally coordinated to the nitrogen atoms of the four 4-methylpyridine ligands and to the two isothiocyanate groups. The Ni - N distances differ not only between the two isothiocyanate (Ni - N(1) = 2,07Å) and the 4-methylpyridine groups, but also between the two symmetrically independent 4-methylpyridine groups (Ni - N(11) = 2,17Å; Ni - N(21) = 2,13Å).

TABLE 4.4 FRACTIONAL ATOMIC COORDINATES (Å x 10^4) AND ISOTROPIC THERMAL MOTION PARAMETERS (Å^2 x 10^3) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom (Host)	*x/a*	*y/b*	*z/c*	U_{iso}
Ni(1)	0(0)	5000(0)	4271(1)	a
N(1)	699(4)	5984(4)	4247(3)	63(2)
C(1)	946(4)	6607(4)	4237(3)	53(2)
S(1)	1315(2)	7478(1)	4208(1)	a
N(11)	-708(3)	5541(3)	3626(3)	55(2)
C(12)	-378(5)	5920(4)	3209(3)	59(2)
C(13)	-793(4)	6276(4)	2786(4)	61(2)
C(14)	-1586(4)	6258(5)	2795(3)	61(2)
C(15)	-1939(5)	5881(5)	3237(4)	66(2)
C(16)	-1484(4)	5532(4)	3637(3)	59(2)
C(17)	-2067(6)	6649(6)	2333(4)	86(3)
N(21)	725(4)	4519(4)	4909(3)	61(2)
C(22)	874(5)	3745(5)	4954(4)	66(2)
C(23)	1353(5)	3435(5)	5382(4)	73(2)
C(24)	1657(5)	3939(5)	5778(4)	70(2)
C(25)	1510(5)	4736(5)	5735(4)	80(3)
C(26)	1036(5)	4995(5)	5304(4)	75(2)
C(27)	2158(6)	3625(6)	6268(4)	94(3)
H(12)	253(5)	5955(4)	3197(3)	b
H(13)	-490(4)	6571(4)	2450(4)	b
H(15)	-2569(5)	5860(5)	3268(4)	b
H(16)	-1771(4)	5236(4)	3980(3)	b

TABLE 4.4 CONT/....

TABLE 4.4 CONTINUED

Atom (Host)	x/a	y/b	z/c	U_{iso}
H(171)	-2691(6)	6735(6)	2359(4)	c
H(172)	-1936(6)	6247(6)	1997(4)	c
H(173)	-1784(6)	7202(6)	2253(4)	c
H(22)	629(5)	3350(5)	4650(4)	b
H(23)	1477(5)	2816(5)	5398(4)	b
H(25)	1756(5)	5140(5)	6034(4)	b
H(26)	905(5)	5611(5)	5283(4)	b
H(271)	2246(6)	3003(6)	6226(4)	c
H(272)	1944(6)	3753(6)	6684(4)	c
H(273)	2706(6)	3925(6)	6202(4)	c
Atom (Guest)				
C(92)	2638(9)	507(8)	4198(5)	d
C(93)	1971(7)	37(10)	4194(5)	d
C(94)	1837(6)	-475(9)	3749(7)	d
C(931)	1411(13)	-12(15)	4677(8)	e
C(932)	1587(29)	-561(27)	5174(17)	e
C(933)	573(18)	224(29)	4496(20)	e

---

[a] Anisotropic thermal parameters defined as in Table 3.4, with parameters;

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni(1)	51(1)	48(1)	58(1)	0(0)	0(0)	-5(1)
S(1)	105(2)	57(1)	99(2)	11(1)	-17(2)	-23(1)

[b] All H atoms have U_{iso} = 99(10)

[c] All H atoms have U_{iso} = 195(26)

[d] All atoms have U_{iso} = 129(3)

[e] All atoms have U_{iso} = 194(5)

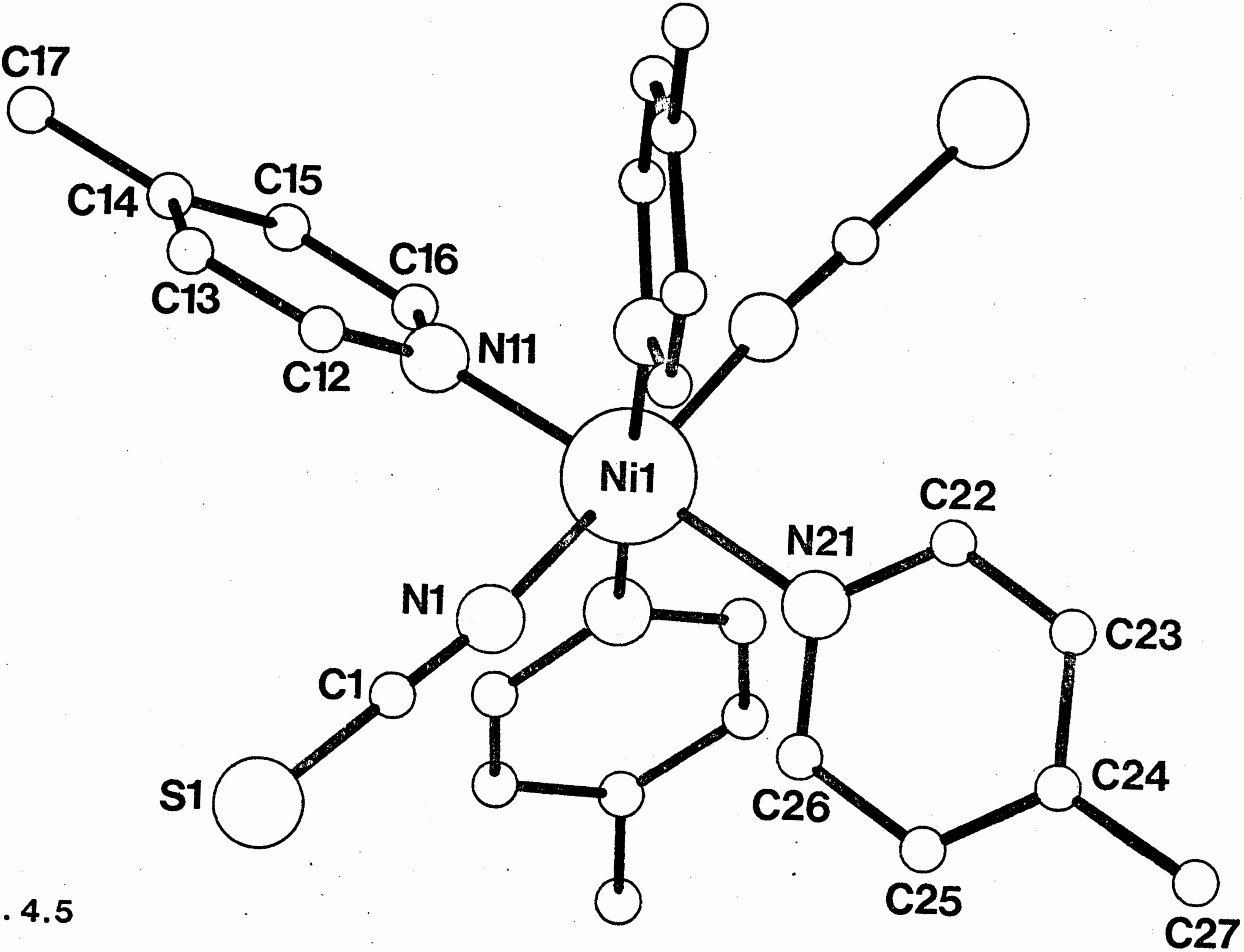

C17
C14
C15
C16
C13
N11
C12
Ni1
C22
N21
N1
C23
C1
C24
S1
C26
C25
C27

FIG. 4.5

TABLE 4.5 BOND LENGTHS (Å) WITH ESTIMATED STANDARD DEVIATION IN PARENTHESES

Host molecule	
Ni(1) - N(1)	2,065(6)
Ni(1) - N(11)	2,165(6)
Ni(1) - N(21)	2,128(6)
N(1) - C(1)	1,147(9)
C(1) - S(1)	1,620(7)
N(11) - C(12)	1,314(9)
N(11) - C(16)	1,328(9)
C(12) - C(13)	1,376(11)
C(13) - C(14)	1,355(10)
C(14) - C(15)	1,376(11)
C(14) - C(17)	1,528(12)
C(15) - C(16)	1,368(11)
N(21) - C(22)	1,353(9)
N(21) - C(26)	1,353(10)
C(22) - C(23)	1,412(11)
C(23) - C(24)	1,380(12)
C(24) - C(25)	1,389(11)
C(24) - C(27)	1,546(13)
C(25) - C(26)	1,381(12)
Guest molecule	
C(92) - C(93)	1,395(0)
C(93) - C(94)	1,395(0)
C(93) - C(931)	1,500(0)

TABLE 4.5 CONT/....

TABLE 4.5 CONTINUED

Guest molecule	
C(931) - C(932)	1,540(0)
C(931) - C(933)	1,551(0)
All C - H bond lengths[a]	1,08

[a] Bond lengths fixed.

TABLE 4.6 BOND ANGLES (DEGREES) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Host Molecule

N(1) - Ni(1) - N(11)	87,5(2)
N(1) - Ni(1) - N(21)	89,8(2)
N(11) - Ni(1) - N(21)	177,3(2)
Ni(1) - N(1) - C(1)	166,2(6)
N(1) - C(1) - S(1)	178,1(7)
Ni(1) - N(11) - C(12)	120,6(5)
Ni(1) - N(11) - C(16)	122,7(5)
C(12) - N(11) - C(16)	116,7(7)
N(11) - C(12) - C(13)	123,4(7)
C(12) - C(13) - C(14)	119,7(8)
C(13) - C(14) - C(15)	117,5(8)
C(13) - C(14) - C(17)	121,2(8)
C(17) - C(14) - C(15)	121,3(7)
C(14) - C(15) - C(16)	119,2(8)
C(15) - C(16) - N(11)	123,4(7)
Ni(1) - N(21) - C(22)	123,0(5)
Ni(1) - N(21) - C(26)	119,6(5)
C(22) - N(21) - C(26)	117,4(7)
N(21) - C(22) - C(23)	122,2(8)
C(22) - C(23) - C(24)	118,6(8)
C(23) - C(24) - C(25)	119,6(8)
C(23) - C(24) - C(27)	120,6(8)
C(27) - C(24) - C(25)	119,8(8)
C(24) - C(25) - C(26)	118,4(9)
C(25) - C(26) - N(21)	123,7(8)

TABLE 4.6 CONT/....

TABLE 4.6 CONTINUED

Guest molecule	
C(92) - C(93) - C(94)	120,0(0)
C(92) - C(93) - C(931)	123,4(0)
C(93) - C(931) - C(932)	119,9(0)
C(93) - C(931) - C(933)	111,2(0)
C(932) - C(931) - C(933)	123,6(0)
C(94) - C(93) - C(931)	116,4(0)

Furthermore, the angles subtended at the nickel atoms are not equivalent. The N(1) - Ni - N(21) angle (89,8(2)^{o}) approximates 90^{o}, whereas the N(1) - Ni - N(11) angle (87,5(2)^{o}) shows a significant 2,3^{o} deviation. The nickel atom lies directly in the N(11), N(21), N(31) and N(41) molecular plane.

The isothiocyanate ligands, with Ni - N - C angles of ∿166,2^{o}, deviate from linearity. Figure 4.6 illustrates the environment of the nickel atom including the isothiocyanate ligands.

The four 4-methylpyridine ligands adopt a windmill conformation. Their aromatic rings are planar to within 0,01Å. The equations of the least squares mean planes and atomic deviations therefrom are listed in Table 4.7. The symmetrically related N(11)- and N(31)-4-methylpyridine ligands are twisted 64^{o} with respect to each other. The N(21)- and N(41)-4-methylpyridine ligands, are similarly twisted but by 69,6^{o} instead. The symmetrically independent N(11)- and N(21)-4-methylpyridine rings deviate by 101,8^{o} from coplanarity. Furthermore, the intramolecular bond lengths of the N(11)-4-methylpyridine ligand are significantly shorter (on average ∿0,2Å) than those of the N(21)-4-methylpyridine ligand.

4.5.2 MOLECULAR PACKING

Illustrations of the packing of the centrosymmetric host molecules in the unit cell, $I4_1/_a$, is shown in Figures 4.7 and 4.8.

The host molecules pack so as to form a closely woven network surrounding channels of void space. Each channel resembles a tube gently bent in the form of a sine wave and constricted by protruding isothiocyanate ligands.

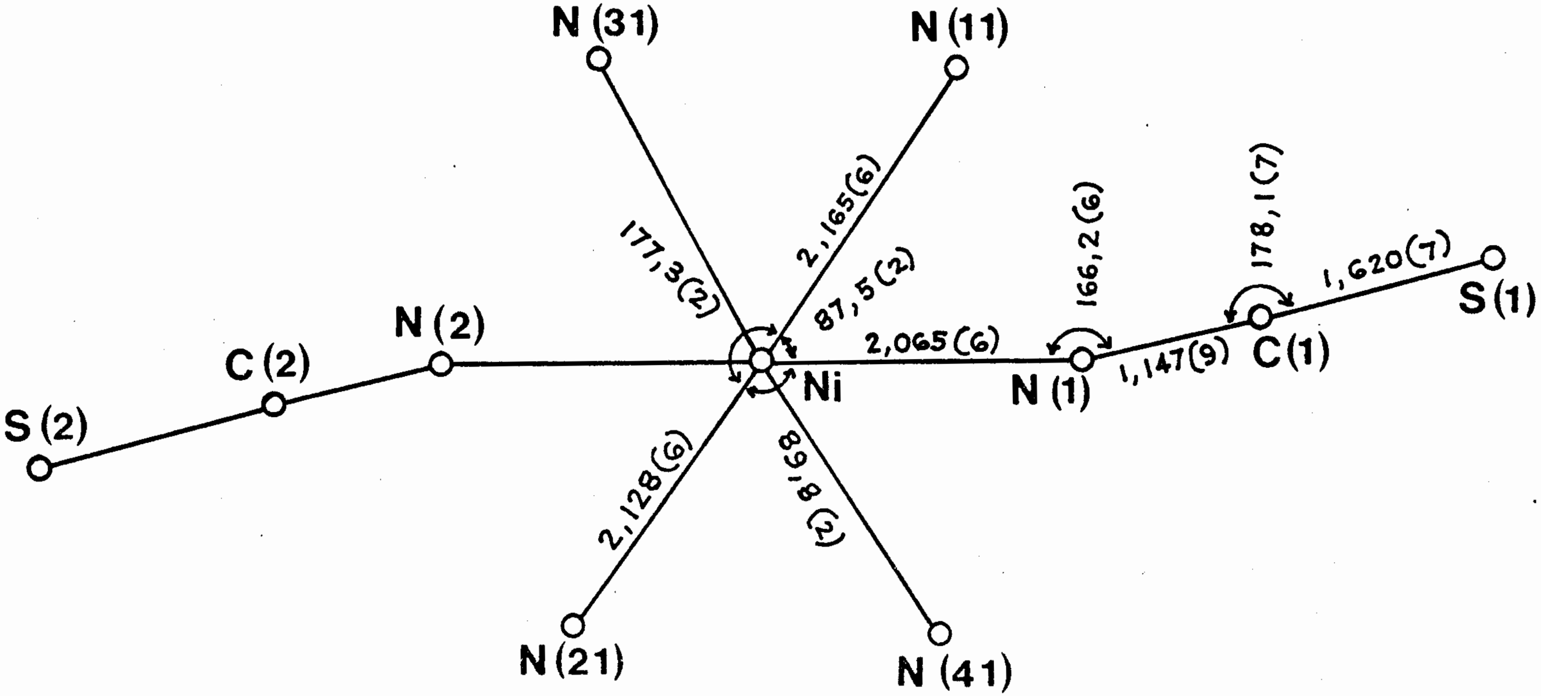


FIGURE 4.6 The environment of the nickel atom including the isothiocyanate ligands. Distances (Å) and angles (°) are shown for the asymmetric unit only.

TABLE 4.7 LEAST SQUARES PLANES AND TORSION ANGLES

---

1 (a) Equations of least-squares planes are expressed in orthogonalised space as $pX + qY + rZ = S$.

Plane 1 : The pyridine ring atoms (N(21), C(22), C(23), C(24), C(25), C(26))

$13,8897X + 2,1018Y - 13,5992Z = -4,7256$

Plane 2 : The pyridine ring atoms (N(41), C(42), C(43), C(44), C(45), C(46))

$13,8897X + 2,1018Y + 13,5992Z = 6,8274$

Plane 3 : The pyridine ring atoms (N(11), C(12), C(13), C(14), C(15), C(16))

$-0,1389X + 14,5037Y + 12,6341Z = 12,6353$

Plane 4 : The pyridine ring atoms (N(31), C(32), C(33), C(34), C(35), C(36))

$-0,1389X + 14,5037Y -12,6341Z = 1,8684$

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

$9,9544X + 13,9095Y - 0,0Z = 6,9547$

Plane 6 : The aromatic ring atoms (C(90), C(91), C(92), C(93), C(94), C(95))

$8,7184X - 12,1707Y + 11,5280Z = 6,5026$

TABLE 4.7 CONT/....

(b) Deviations from the planes (Å x 10^3)

(σ x 10^3 < 20)

Atom	*Plane 1*	*Atom*	*Plane 2*
N(11)	-20	N(11)	-1711
N(21)*	8	N(21)	1806
C(22)*	-7	N(31)	20
C(23)*	-11	N(41)*	-8
C(24)*	-6	C(42)*	7
C(25)*	6	C(43)*	-6
C(26)*	-7	C(44)*	6
C(27)	-40	C(45)*	-6
N(31)	1711	C(46)*	7
N(41)	-1806	C(47)	40
Ni(1)	-32	Ni(1)	32
C(90)	4411	C(90)	1948

Atom	*Plane 3*	*Atom*	*Plane 4*
N(11)*	-12	N(11)	1593
C(12)*	10	N(21)	-1531
C(13)*	-1	N(31)*	12
C(14)*	-9	C(32)*	-10
C(15)*	7	C(33)*	1
C(16)*	3	C(34)*	9
C(17)	-22	C(35)*	-7
N(21)	105	C(36)*	-3
N(31)	-1593	C(37)	22
N(41)	1531	N(41)	-105
Ni(1)	125	Ni(1)	-13
C(90)	-8447	C(90)	-6124

TABLE 4.7 CONT/....

Atom	*Plane 5*
N(11)*	48
N(21)*	49
N(31)*	-48
N(41)*	-49
Ni(1)	0
N(1)	2066
N(2)	-2066
C(90)	3915

Atom	*Plane 6*
N(11)	-9678
N(21)	-5706
N(31)	-7138
N(41)	-8152
Ni(1)	-7664
C(90)*	-3
C(91)*	3
C(92)*	-3
C(93)*	3
C(94)*	-3
C(95)*	3

(c) Angles between normals to planes (degrees)

Plane 1 and 2	69,6
Plane 1 and 3	101,8
Plane 1 and 4	66,4
Plane 1 and 5	55,1
Plane 1 and 6	87,1
Plane 2 and 3	66,4
Plane 2 and 4	101,8
Plane 2 and 5	55,1
Plane 2 and 6	53,0
Plane 3 and 4	64,0
Plane 3 and 5	46,8
Plane 3 and 6	110,6
Plane 4 and 5	46,8
Plane 4 and 6	149,8
Plane 5 and 6	106,4

TABLE 4.7 CONT/....

2 Selected torsion angles (degrees). The torsion angle $\omega(I\text{-}J\text{-}K\text{-}L)$ is defined as the angle between the vector $J\text{-}I$ and the vector $K\text{-}L$ when viewed down $J\text{-}K$. The sign of ω is positive if $J\text{-}I$ is to be rotated clockwise into $K\text{-}L$ and negative if anticlockwise[64].

N(1) - Ni(1) - N(21) - C(26)	37,2
N(1) - Ni(1) - N(41) - C(42)	32,2
N(21) - Ni(1) - N(11) - C(12)	44,4
N(21) - Ni(1) - N(31) - C(32)	133,1
N(11) - Ni(1) - N(21) - C(26)	33,6
N(11) - Ni(1) - N(41) - C(42)	-55,3

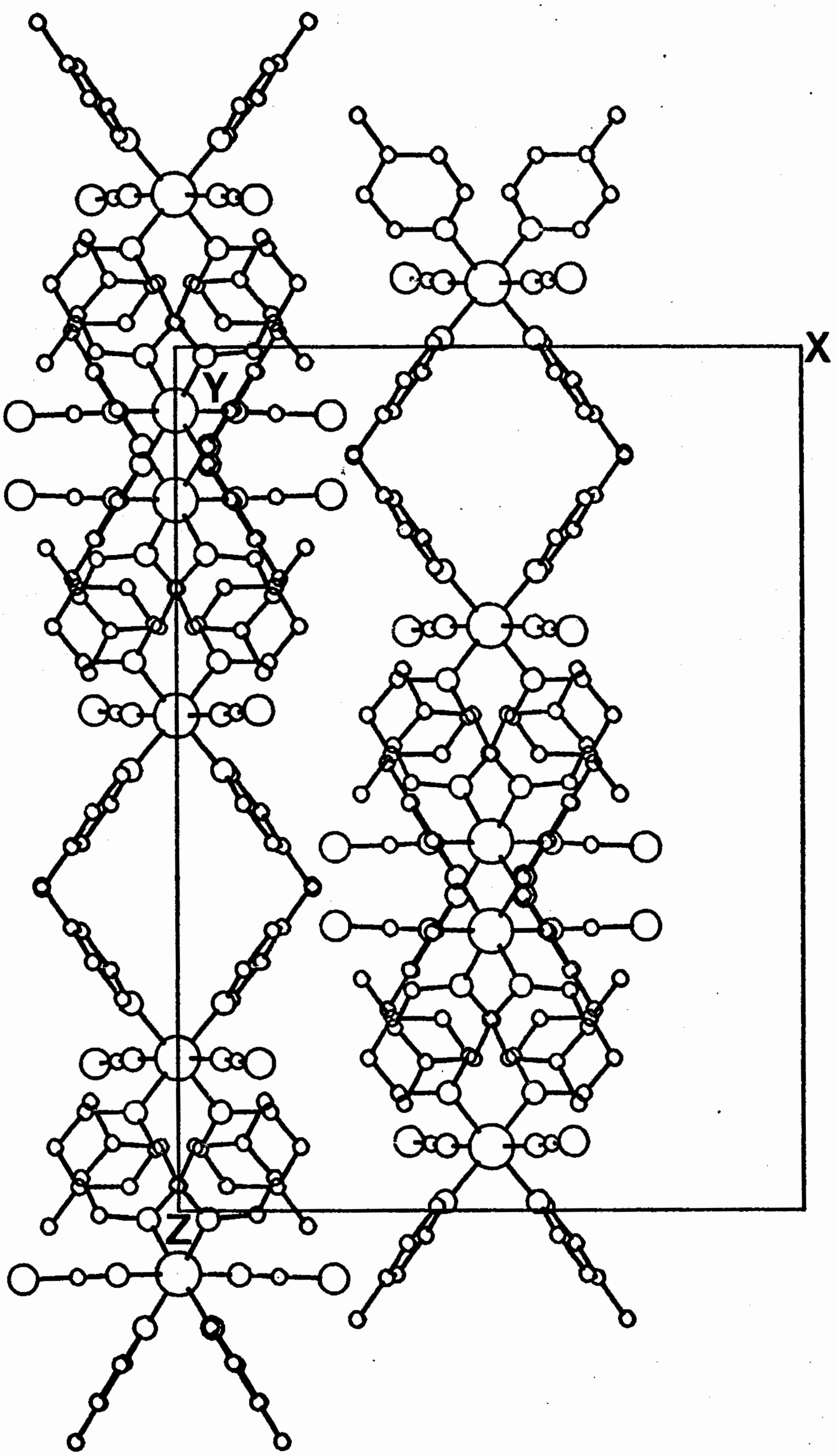


FIGURE 4.7 An illustration of the packing of the host molecules in the unit cell.

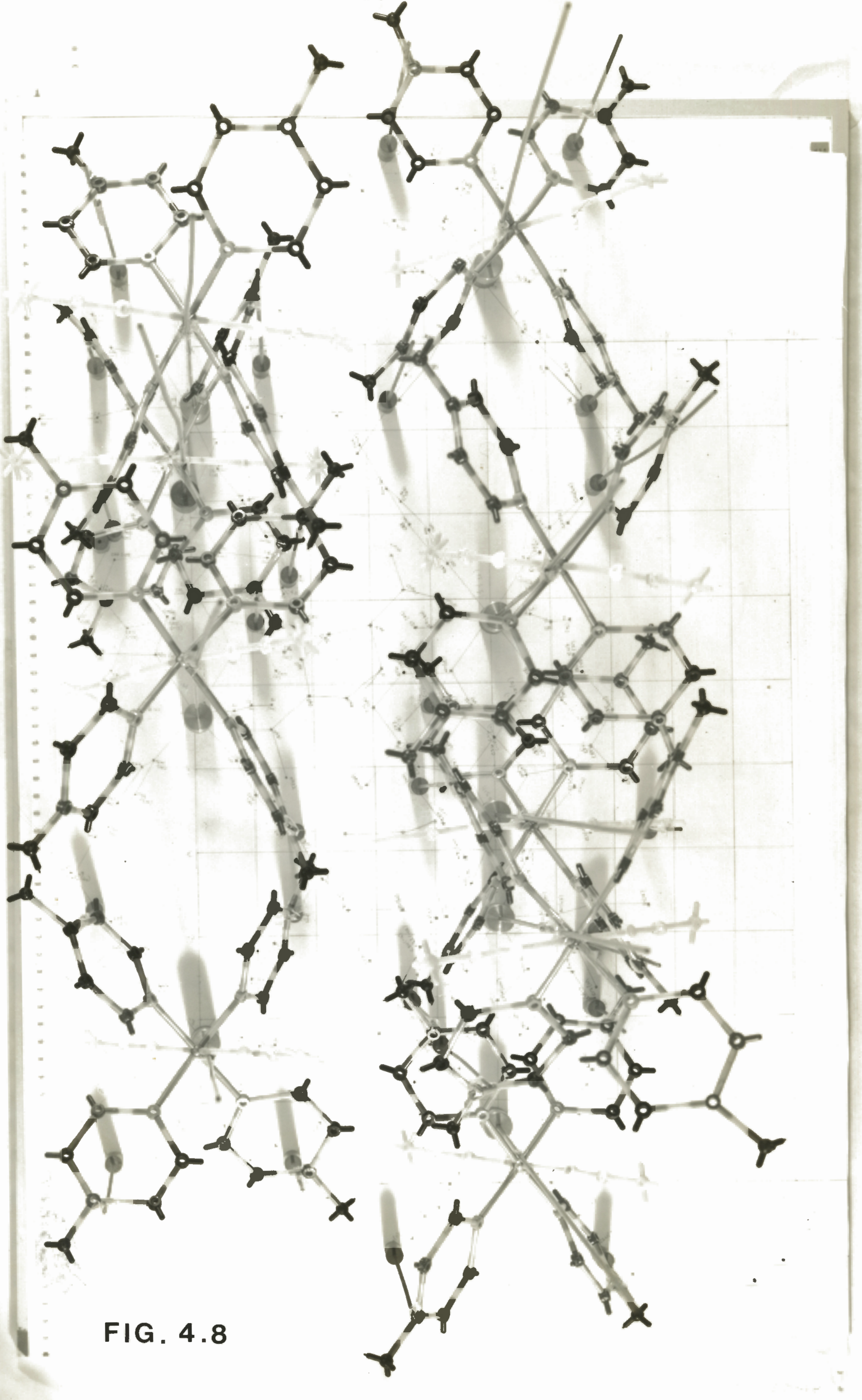


FIG. 4.8

Three-dimensional sets of cavities are thus created wherein the guest molecules are fitted. Each cavity contains a centre of inversion on which the non-centrosymmetric p-cymene molecule is positioned. The p-cymene molecule is disordered in order to meet the symmetry requirement. Viewing down the *y* axis (See Figure 4.9) it would at first appear as if there are two different cavities available for guest occupation. However the "diamond-shaped" cavities and the "tube-like" channel are crystallographically equivalent and both are filled by the p-cymene molecules. Figure 4.10 illustrates the packing of the p-cymene molecules in the cavities. The p-cymene molecules are planar to within experimental error. Furthermore they do not lie coplanar with any one of the 4-methylpyridine rings.

The estimated dimensions of the cavities are 4,6 x 7,0 x 16,8Å. The p-cymene molecule, measured with van der Waal's radii has approximate dimensions of 4,6 x 5,8 x 10,8Å and is therefore closely moulded in its cavity. The limiting cross-sections of these channels (4,6 x 7,0Å) are larger than those reported for the β-phase benzene clathrate[56] (3,3 x 6,8Å). This suggests that dilation of the host lattice occurred in order to meet the demands of the larger guest molecule, p-cymene.

The presence of an aromatic hydrocarbon thus transforms the non-clathrate α-phase host complex into a relatively stable β-phase clathrate. Guarino *et al*[36] have proposed charge-transfer interactions between aromatic guest and host molecules to account for their stability. They maintain, "the site occupied by the guest provokes a specific orientation of the picoline molecules and consequently a specific coupling between them and the guests give rise to different host-host and host-guest interactions". However this charge-transfer hypothesis is not confirmed by the present study. Parallelism of the p-cymene molecule with any one of the aromatic rings in

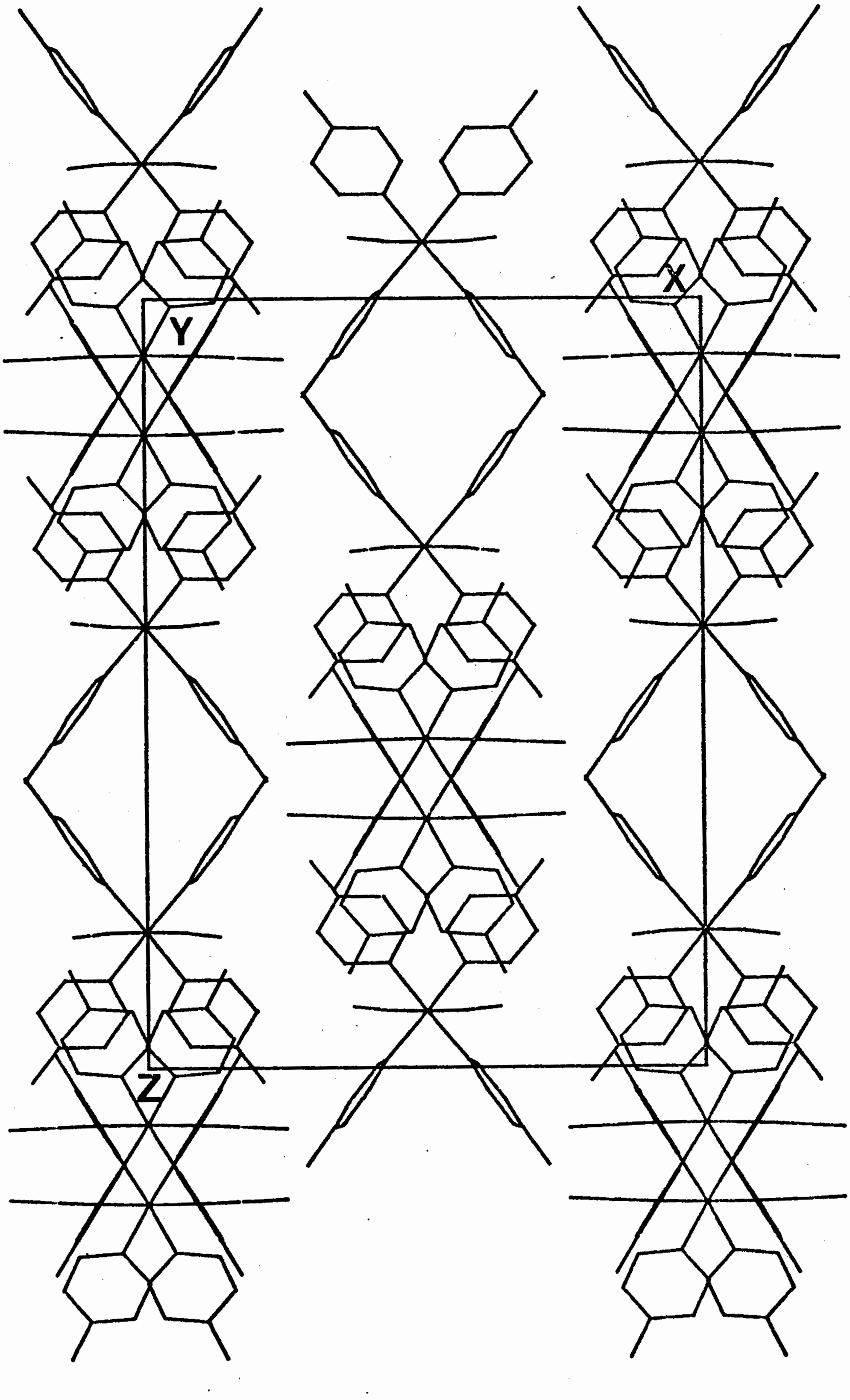


FIGURE 4.9 The channels viewed down the y axis.

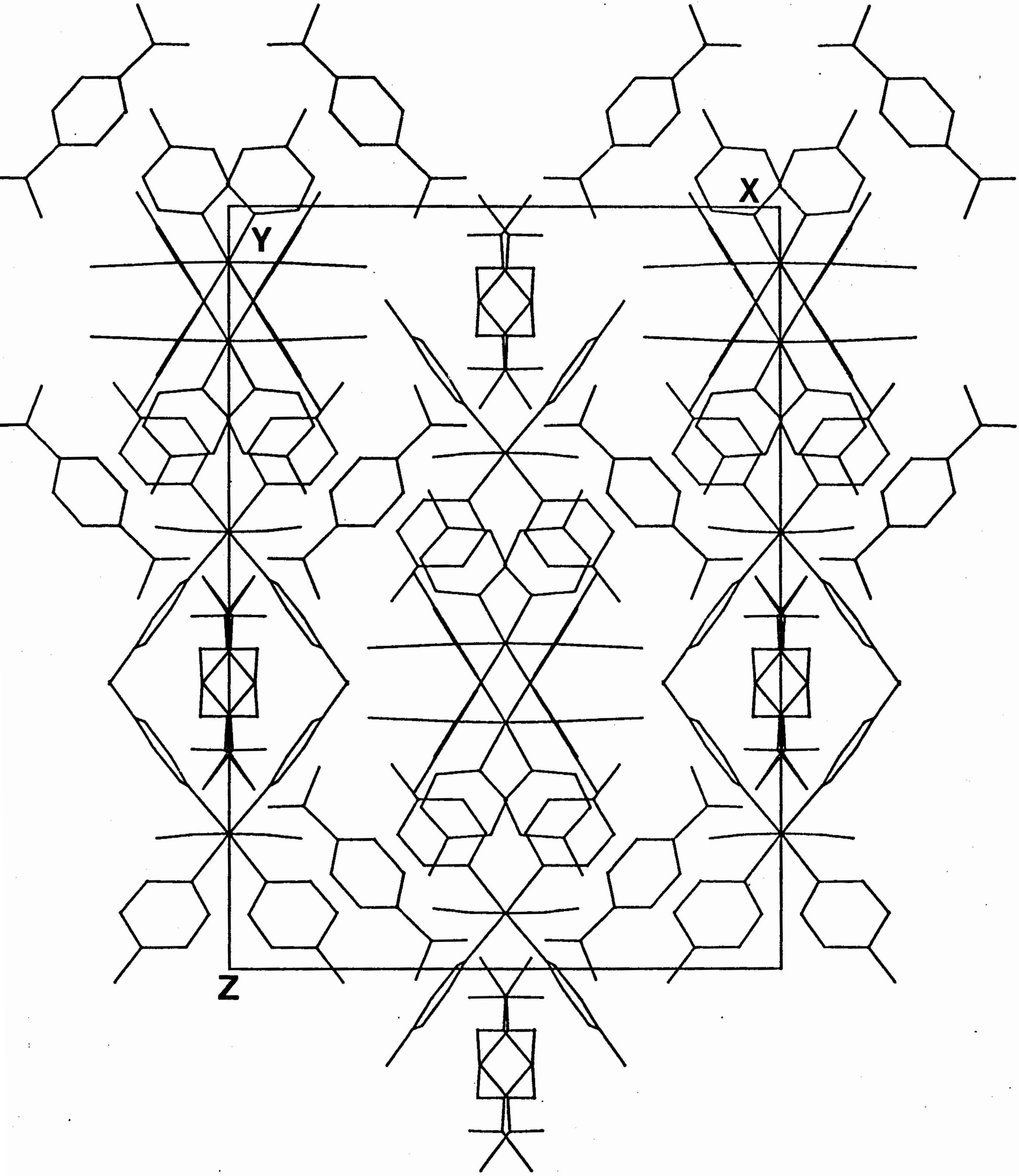


FIGURE 4.10 An illustration of the packing of the p-cymene molecules in the cavities.

the host lattice does not occur. Shortening of intermolecular distances with respect to the sum of the van der Waal's radii is not observed. Furthermore, confirmation as to the absence of specific chemical guest-host interactions (in solution) is obtained from a ^{1}H N.M.R. study of the p-cymene clathrate (See Chapter 5).

4.6 A CONFORMATIONAL STUDY OF THE 4-METHYLPYRIDINE LIGANDS

The conformational flexibility of the four 4-methylpyridine ligands allows the $Ni(NCS)_2(4\text{-MePy})_4$ complex to "adjust" its molecular shape in order to enclathrate guest molecules differing in shape and size.

It should therefore be possible to predict the type of guest species to be preferentially enclathrated once the conformation of the host complex is known.

From intramolecular non-bonded energy calculations, the overall conformation of the complex was determined. As in section 3.6, non-bonded interactions were calculated using potential functions $U(r)$ expressed as;

$$U(r) = a\exp(-br)/r^d - c/r^6$$

The solved p-cymene clathrate structure provided the input data for the geometry of the $Ni(NCS)_2(4\text{-MePy})_4$ molecule. The energy sum was calculated as a function of torsion angles; N(1) - Ni - N(x) - C(y) with x = 11 and y = 12 (τ_1), x = 21 and y = 26 (τ_2), x = 41 and y = 42 (τ_3) and x = 31 and y = 36 (τ_4) suitably defining torsion of the respective pyridine rings from the N(11), N(21), N(31) and N(41) molecular plane. (Refer to Figure 4.5)

Figure 4.11 illustrates the result concerning non-bonded interactions of the two symmetrically independent N(21)- and N(31)-4-methylpyridine ligands

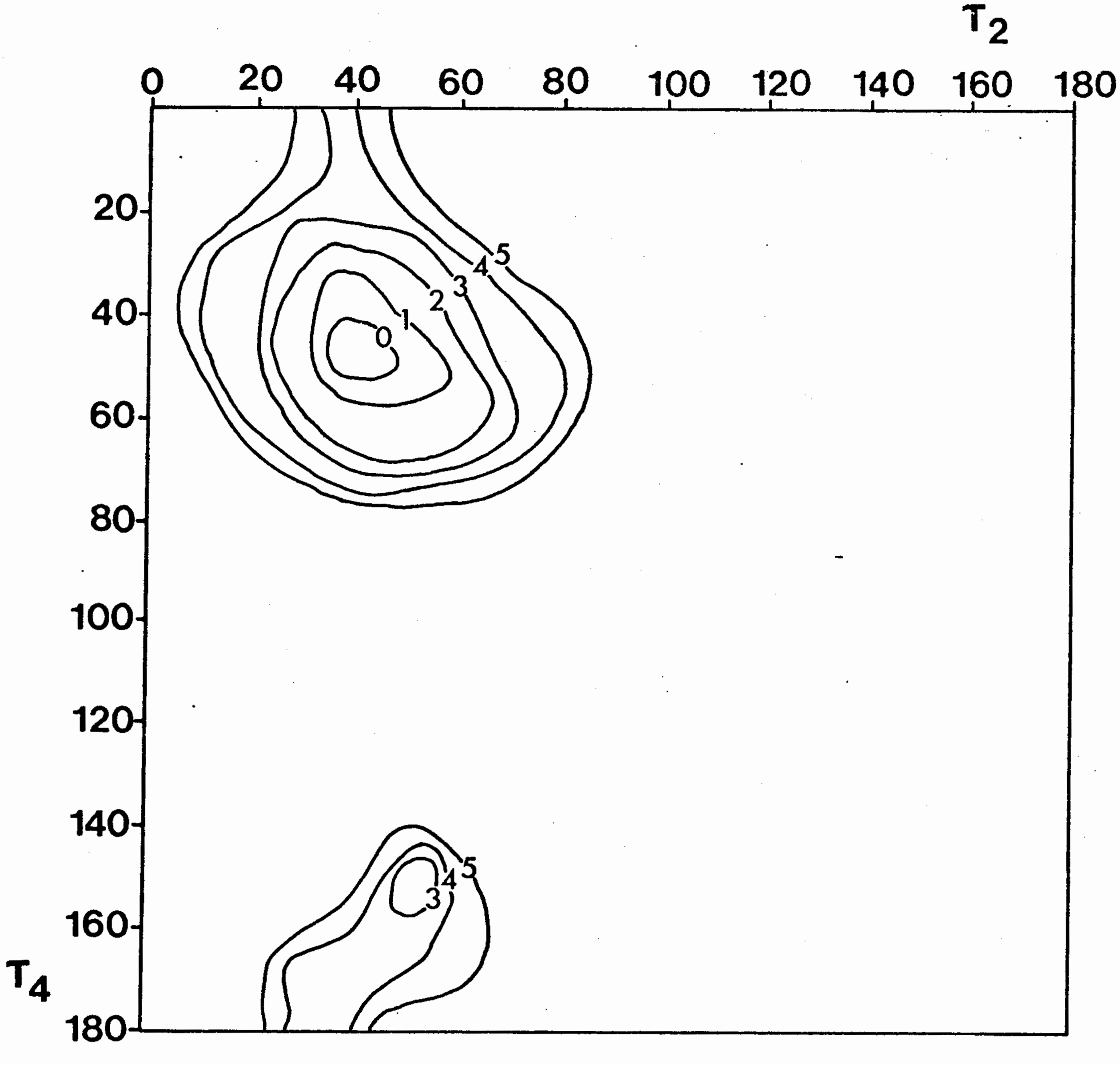


FIGURE 4.11 A Layer Diagram of van der Waal's energy (kcal) of interaction between the N(21) and N(31) 4-methylpyridine ligands and the N(1) - Ni(1) - N(2) subunit.

and the N(2) - Ni - N(1) subunit. A deep minimum occurs at $\tau_2 = 37^o$ and $\tau_4 = 46^o$. This minimum energy region may be regarded as corresponding to a (++) conformation of the 4-methylpyridine ligands. When a two-fold axis is diagonal between the 4-methylpyridine ligands as observed in the tetragonal β-phase p-cymene clathrate, the torsion angles are restricted by imposing $\tau_1 = \tau_4$ and $\tau_2 = \tau_3$. Thus non-bonded interactions between the two symmetrically independent N(11) and N(41) 4-methylpyridine ligands plotted as a function of τ_1 and τ_3 should yield similar results. A subsequent layer diagram of van der Waal's energy plotted as a function of τ_1 and τ_3 produced a minimum at $\tau_1 = 41^o$ and $\tau_3 = 32^o$. Assuming that the overall conformation of the 4-methylpyridine ligands is determined by the sum of interactions of neighbouring 4-methylpyridine ligands, a (++++) type conformation of the pyridine molecular planes is obtained. This (++++) type is the so-called windmill conformation as mentioned in Section 4.5.

Thus the host in the p-cymene clathrate has a (++++) conformation with averaged torsion angle values; $\tau_1 = \tau_4 = 43,19^o$ and $\tau_2 = \tau_3 = 34,74^o$.

These values compare favourably with those averaged for five known β-structures. Lipkowski[57] quotes the average values for $\tau_1 = \tau_4$ as 43^o and $\tau_2 = \tau_3$ as 34^o.

and the N(2) - Ni - N(1) subunit. A deep minimum occurs at $\tau_2 = 37^\circ$ and $\tau_4 = 46^\circ$. This minimum energy region may be regarded as corresponding to a (++) conformation of the 4-methylpyridine ligands. When a two-fold axis is diagonal between the 4-methylpyridine ligands as observed in the tetragonal β-phase p-cymene clathrate, the torsion angles are restricted by imposing $\tau_1 = \tau_4$ and $\tau_2 = \tau_3$. Thus non-bonded interactions between the two symmetrically independent N(11) and N(41) 4-methylpyridine ligands plotted as a function of τ_1 and τ_3 should yield similar results. A subsequent layer diagram of van der Waal's energy plotted as a function of τ_1 and τ_3 produced a minimum at $\tau_1 = 41^\circ$ and $\tau_3 = 32^\circ$. Assuming that the overall conformation of the 4-methylpyridine ligands is determined by the sum of interactions of neighbouring 4-methylpyridine ligands, a (++++) type conformation of the pyridine molecular planes is obtained. This (++++) type is the so-called windmill conformation as mentioned in Section 4.5.

Thus the host in the p-cymene clathrate has a (++++) conformation with averaged torsion angle values; $\tau_1 = \tau_4 = 43{,}19^\circ$ and $\tau_2 = \tau_3 = 34{,}74^\circ$.

These values compare favourably with those averaged for five known β-structures. Lipkowski[57] quotes the average values for $\tau_1 = \tau_4$ as 43° and $\tau_2 = \tau_3$ as 34°.

CHAPTER 5

CHAPTER 5

A PROTON NUCLEAR MAGNETIC RESONANCE STUDY OF THE BENZENE AND P-CYMENE CLATHRATES

5.1 INTRODUCTION

Nuclear relaxation studies provide kinetic and structural information. In the presence of certain paramagnetic ions, the longitudinal relaxation times (T_1's) of nearby nuclei provide a sensitive probe as to molecular structure.

Williams *et al*[58] have determined the conformations of penicillins, amino-acids, small peptides, sugars, nucleotides and various other drug molecules in solution employing paramagnetic probes. Recently, the intramolecular ring-stacking interaction between caffeine and the paramagnetic bis(phenanthroline)copper(II) cation[59] has been investigated.

However this technique has to date not been employed in clathrate conformational studies. We thus investigated the clathrate system in solution following a similar procedure to that of the ring-stacking study[59]. (They employed the Cu(II) ion as probe, which broadens resonances, whereas in our study the paramagnetic Ni(II) ion was used as probe. The Ni(II) ion shifts the resonances rather than broadens them.)

The β-phase benzene clathrate structure, previously solved by de Gil and Kerr[56] provided a system on which to experiment. Thereafter the β-phase p-cymene clathrate system was investigated in order to determine the association constant K and to calculate the internuclear distance r, between host and guest molecules in solution.

A knowledge of the interactions occurring in solution may provide a better understanding as to the formation of a clathrate structure.

5.2 THEORY

Basic N.M.R. relaxation theory is dealt with in depth by Dwek[60]. Therefore, only a short résumé fo the aspects pertinent to this study are given.

Solomon and Bloembergen have formulated an expression for the relaxation time (T_1) of a nucleus near a paramagnetic ion, as follows;

$$\frac{1}{T_{1M}} = \frac{2}{15} \frac{\gamma_I^2 g^2 S(S+1) \beta^2}{r^6} \left[\frac{3 \tau_c}{1 + \omega_I^2 \tau_c^2} + \frac{7 \tau_c}{1 + \omega_S^2 \tau_c^2} \right] \quad \ldots.(1)$$

where r is the distance between the nucleus and the paramagnetic ion (*i.e.* the internuclear distance) and τ_c, the correlation time modulating the interaction. For a system involving a Ni(II) ion, this is dominated by the electronic relaxation time of the metal. Other parameters con= tributing to the $1/T_{1M}$ value are S, the total electron spin, ω_S and ω_I, the electronic and nuclear Larmor precession frequencies, γ_I, the magneto= gyric ratio and β, the Bohr magnetron.

Furthermore the hyperfine coupling constant ($A/\hbar$) has been ignored, because Ni(II) hyperfine contact interactions are large in the presence of covalent bond formation only, which in our system is absent. However, the chemical shifts and relaxation times of the host nuclei are dominated by pseudo-contact interactions.

By inserting the appropriate constants into the Solomon-Bloembergen equation with a correlation time, τ_c, equal to 3×10^{-12} seconds equation (1) reduces to,

$$\frac{1}{T_{1M}} = \frac{1{,}32 \times 10^{-42}}{r^6} \qquad \text{....(2)}$$

Thus if the $1/T_{1M}$ value is known, the internuclear distance r, can be calculated. An objective of this study is to determine the internuclear distance r, between guest and host molecules.

In solution, the guest species will not be enclathrated at all times, instead a dynamic equilibrium will exist between the enclathrated and the free guest. If the exchange is rapid, the observed relaxation may be averaged as follows,

$$\frac{1}{T_{1(obs)}} = \frac{f}{T_{1M}} + \frac{1 - f}{T_{1A}} \qquad \text{....(3)}$$

where T_{1M} is the relaxation time of the enclathrated guest, T_{1A}, the relaxation time of the free guest and f, the mole fraction of the "captive" guest.

The clathration process may simply be represented as,

$$\text{Host (H)} + \text{Guest (G)} \rightleftharpoons \text{Host.Guest (H.G.)}.$$

Therefore the equilibrium constant $K = [HG]/[H].[G]$

Furthermore, the total guest concentration,

$$T_G = [HG] + [G] = K[H].[G] + [G]$$

and the total host concentration,

$$T_H = [HG] + [H] = K[H].[G] + [H].$$

The mole fraction of enclathrated guest, $f = [HG]/T_G$ ....(4)

The observed relaxation time, $1/T_{1(obs)}$, can therefore be related to the equilibrium constant K by the appropriate substitution. The constants, T_{1M} and K may therefore be solved from a series of simultaneous equations. Alternatively, T_{1M} and K may be solved by an iterative procedure where the theoretical $T_{1(obs)}$ is calculated and compared with the experimentally obtained value. The values of T_{1M} and K giving a minimum square error sum are assumed correct.

However if $T_G \gg T_H$, then [G] may be simplified to T_G and $1 - f \simeq 1$. The observed relaxation may now be expressed as,

$$\frac{1}{T_{1P}} = \frac{1}{T_{1(obs)}} - \frac{1}{T_{1A}} = \frac{T_H K}{T_G K + 1} \cdot \frac{1}{T_{1M}} \qquad \text{....(5)}$$

or $T_{1P}\, T_H = T_{1M}/K + T_{1M}\, T_G$.

A plot of $T_{1P}\, T_H$ versus T_G should yield a straight line with slope T_{1M} and intercept T_{1M}/K.

Since the effect of the paramagnetic Ni(II) ion on the guest species is not as great as on a molecule directly bonded to the metal ion and due to the high concentration of Ni^{2+} present, outer-sphere relaxation must be taken into account. The outer-sphere relaxation time for Ni(II) and Co(II) (where the electron spin relaxation time is of importance) may be given by;

$$\frac{1}{T_{1A}''} = \frac{2}{15} N_s \gamma_I^2 g^2 S(S+1) \beta^2 \left[\frac{3\tau_c}{1+\omega_I^2 \tau_c^2} + \frac{7\tau_c}{1+\omega_s^2 \tau_c^2} \right] \frac{\pi}{d^3} \quad \ldots.(6)$$

where, N_s is the number of spins per ml of solution, d, the radius of closest approach and the other parameters are as explained previously.

Under the experimental conditions of 21,35G and a host concentration of 0,4mol.dm^{-3}, the contribution of outer-sphere relaxation to the total relaxation time is 0,7 seconds (where d = 9Å and $\tau_c = 3 \times 10^{-12}$ sec.).

5.3 RESULTS AND DISCUSSION

5.3.1 BENZENE CLATHRATE SYSTEM

The ^{1}H N.M.R. spectrum of the $Ni(NCS)_2(4\text{-MePy})_4$.benzene clathrate contained a single benzene resonance. The paramagnetic Ni^{2+} ion shifted the 4-methylpyridine resonances from their normal resonance positions and they were not observed in the normal 1000kHz range. The results of the relaxation study of this clathrate system is given in Table 5.1. (The $1/T_{1(obs)}^*$ values tabulated have been corrected for the diamagnetic contribution and outer-sphere relaxation.) A plot of $1/T_{1(obs)}^*$ as a function of [Benzene]/[Host] is given in Figure 5.1. Superimposed is the theoretical curve determined with T_{1M} = 0,015 and K = 8,0.

The experimental and the theoretical curve show good correlation within experimental error, however the experimental curve does deviate systematically. In order to improve the fit a more complex non-cooperative association was considered, *i.e.*

$$2\ \text{Host} + \text{Guest} \rightleftharpoons (\text{Host})_2\text{Guest}$$

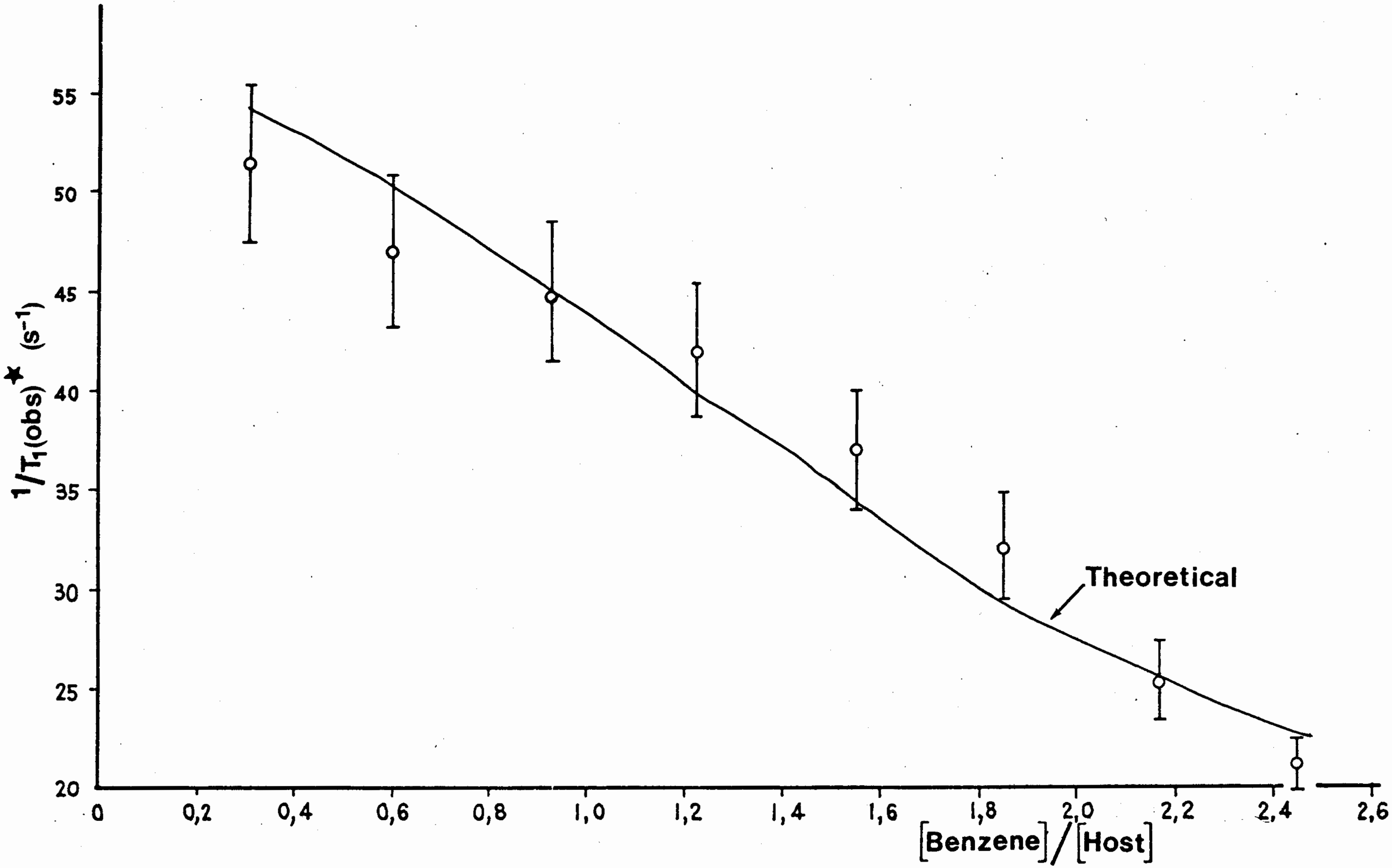


FIGURE 5.1 A plot of $1/T_{1(obs)}{}^{*}$ as a function of [Benzene]/[Host]

Although this increased the complexity of the system dramatically, it did not improve the correlation significantly. We concluded that the 1 : 1 system, *i.e.*

$$\text{Host} + \text{Guest} \rightleftharpoons \text{Host.Guest}$$

was the best description for the association and interpreted the deviation as due to (1) incomplete clathrate formation and (2) more complex species existing in solution.

The significance of these results will be discussed in conjunction with results obtained from the p-cymene study.

TABLE 5.1 BENZENE CLATHRATE RELAXATION STUDY

Aromatic protons: $1/T_{1A} = 0,17s^{-1}$

[HOST]	[BENZENE]	$\frac{\text{[BENZENE]}}{\text{[HOST]}}$	$\frac{1}{T_{1(obs)}}$*
$mol.dm^{-3}$	$mol.dm^{-3}$		s^{-1}
0,72	0,22	0,31	51,3 (±4,1)
0,70	0,43	0,61	46,9 (±3,8)
0,69	0,64	0,93	44,9 (±3,6)
0,68	0,83	1,22	42,0 (±3,4)
0,66	1,02	1,55	37,0 (±3,0)
0,48	0,89	1,85	32,2 (±2,6)
0,47	1,02	2,17	25,4 (±2,0)
0,47	1,15	2,45	21,2 (±1,7)

*$1/T_{1(obs)}$ has been corrected for the diamagnetic contribution and outer-sphere relaxation.

5.3.2 P-CYMENE CLATHRATE SYSTEM

The ^{1}H N.M.R. spectrum of the Ni(NCS)$_2$(4-MePy)$_4$.p-cymene clathrate is shown in Figure 5.2. The assignment of the spectrum is given in Section 4.1. Considerable shifting of the 4-methylpyridine resonances from their normal resonance positions occurred. However the chemical shift of the guest molecule, p-cymene, is independent of host concentration. This would imply that the p-cymene molecules are not covalently bonded to the host molecules.

The results of the relaxation study are given in Table 5.2. These show that the longitudinal relaxation times of the p-cymene resonances are dependent on host concentration. However, the relaxation times of the four resonances of the p-cymene molecule do not differ significantly. The p-cymene hydrogen atoms are thus equidistant with respect to the paramagnetic centre, *i.e.* they have the same dependence on host concen=tration. We thus conclude that the p-cymene molecule has no specific orientation but undergoes rapid conformational "flipping" in solution. This proposal is in accordance with the crystallographic study which predicts a disordered p-cymene molecule.

The observed relaxation time ($1/T_{1(obs)}{}^*$) for the arbitrarily chosen resonance integrating for the dimethyl moiety (Peak 4) was plotted as a function of [Host]/[p-Cymene]. (See Figure 5.3) Superimposed is the theoretical curve obtained for T_{1M} = 0,014 and K = 2,0. The fit is within experimental error.

The equilibrium constant K, determined as 8,0±1M^{-1} and 2,0±1M^{-1} for the benzene and p-cymene clathrate system respectively, indicates that some association between the guest molecules and the host lattice must be

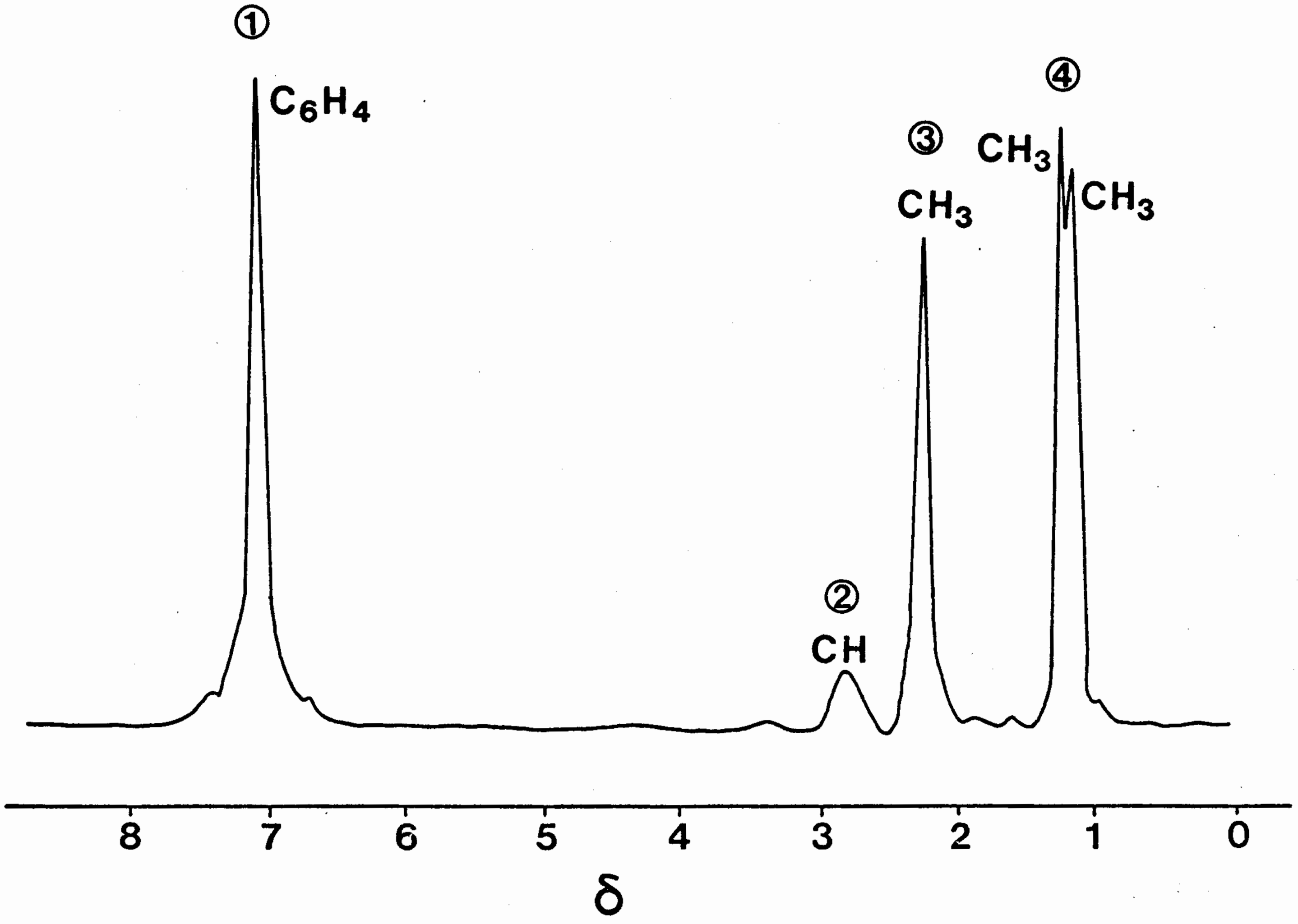


FIGURE 5.2 The ^{1}H N.M.R. spectrum of the p-cymene clathrate illustrating the p-cymene resonances only. See Figure 4.2 for the entire ^{1}H N.M.R. spectrum of the p-cymene clathrate.

TABLE 5.2 P-CYMENE CLATHRATE RELAXATION STUDY

$1/T_{1A} = 0{,}37s^{-1}$

PEAK 1 Aromatic Protons

[HOST]	[P-CYMENE]	$\frac{[HOST]}{[P\text{-}CYMENE]}$	$\frac{1}{T_{1(obs)}}$*
$mol.dm^{-3}$	$mol.dm^{-3}$		s^{-1}
0,10	0,91	0,11	6,3 (±0,5)
0,18	0,80	0,23	8,3 (±0,7)
0,29	0,64	0,45	15,3 (±1,2)
0,33	0,58	0,57	18,8 (±1,5)
0,36	0,53	0,68	27,6 (±2,2)
0,39	0,50	0,78	25,3 (±2,0)
0,42	0,46	0,91	30,5 (±2,4)

PEAK 2 Methine Proton

[HOST]	[P-CYMENE]	$\frac{[HOST]}{[P\text{-}CYMENE]}$	$\frac{1}{T_{1(obs)}}$*
$mol.dm^{-3}$	$mol.dm^{-3}$		s^{-1}
0,10	0,91	0,11	4,4 (±0,4)
0,18	0,80	0,23	9,4 (±0,8)
0,29	0,64	0,45	16,5 (±1,3)
0,33	0,58	0,57	16,7 (±1,3)
0,36	0,53	0,68	18,7 (±1,5)
0,39	0,50	0,78	23,6 (±1,9)
0,42	0,46	0,91	23,5 (±1,9)

TABLE 5.2 CONT/....

PEAK 3 Methyl Protons

[HOST]	[P-CYMENE]	$\frac{[HOST]}{[P\text{-}CYMENE]}$	$\frac{1}{T_{1(obs)}}$*
$mol.dm^{-3}$	$mol.dm^{-3}$		s^{-1}
0,10	0,91	0,11	6,5 (±0,5)
0,18	0,80	0,23	8,6 (±0,7)
0,29	0,64	0,45	16,8 (±1,3)
0,33	0,58	0,57	17,0 (±1,4)
0,36	0,53	0,68	23,7 (±1,9)
0,39	0,50	0,78	32,2 (±2,6)
0,42	0,46	0,91	27,1 (±2,2)

PEAK 4 Dimethyl Protons

[HOST]	[P-CYMENE]	$\frac{[HOST]}{[P\text{-}CYMENE]}$	$\frac{1}{T_{1(obs)}}$*
$mol.dm^{-3}$	$mol.dm^{-3}$		s^{-1}
0,10	0,91	0,11	5,0 (±0,4)
0,18	0,80	0,23	8,3 (±0,7)
0,29	0,64	0,45	18,9 (±1,5)
0,33	0,58	0,57	17,6 (±1,4)
0,36	0,53	0,68	20,5 (±1,6)
0,39	0,50	0,78	22,6 (±1,8)
0,42	0,46	0,91	27,1 (±2,2)

*$1/T_{1(obs)}$ has been corrected for the diamagnetic contribution and outer-sphere relaxation.

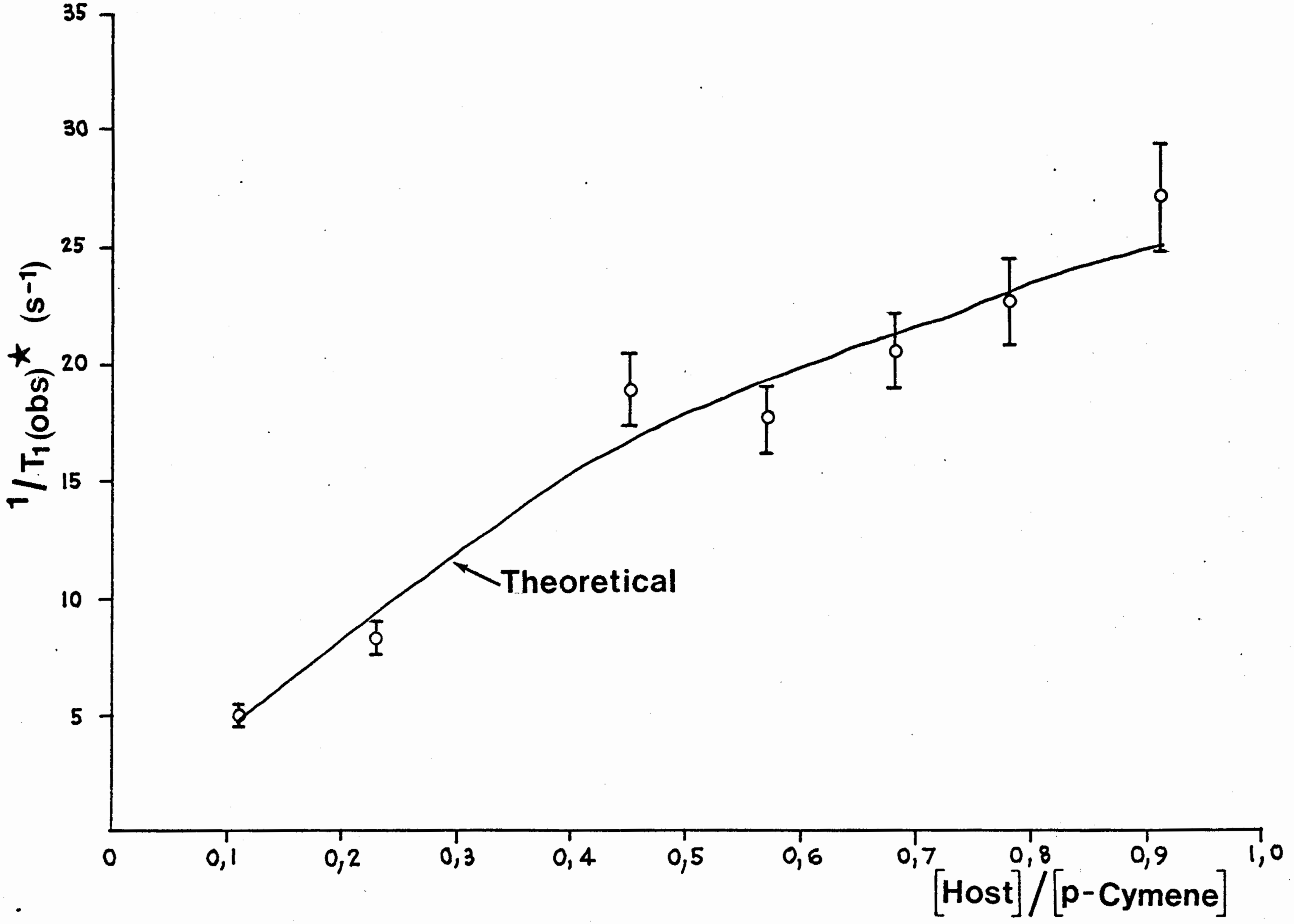


FIGURE 5.3 A plot of $1/T_{1(obs)}^*$ as a function of [Host]/[p-Cymene]

occurring in solution. Furthermore these values of K are of the same order of magnitude as that obtained by Dei *et al*[59]. They estimate the value of K as 9,7±1,8M^{-1} for the ring-stacking interaction and a value of 10,1±1,2M^{-1} for the $Cu(phen)_2$caffeine association constant.

However the association constant K estimated as 8,0 in the benzene clathrate study is greater than the value of 2,0 determined for the p-cymene clathrate system. We propose that the larger, bulkier p-cymene molecule experiences "closer contacts" (*i.e.* greater steric interaction) with the host molecules, hence their lower K value.

The average internuclear distance r, between the protons and the paramagnetic Ni(II) ion was estimated from Equation (2) by substituting the appropriate T_{1M} values. The internuclear distance r, was calculated to be 5,84Å and 5,77Å for the benzene and p-cymene clathrate respectively. The crystallographic proton-metal distances for the p-cymene clathrate are given in Table 5.3. The experimentally determined r value of 5,77Å compares reasonably well with the averaged crystallographic proton-metal distances. However the internuclear distance r, was expected to have a value greater than 5,77Å. A possible source of error may be in the estimation of the correlation time τ_c as 3×10^{-12} seconds. A further explanation as to the discrepancy is based on the fact that the p-cymene protons were assumed to experience an interaction mode with two equidistant paramagnetic Ni(II) ions only. When considering more distant paramagnetic centres, each interacting with the p-cymene protons, then the numerator in Equation (2) will be increased, hence a better estimate for the average internuclear distance may be obtained.

Furthermore, the internuclear distances calculated for the benzene and the p-cymene clathrates do not differ significantly. This would imply that

TABLE 5.3 CRYSTALLOGRAPHIC PROTON-METAL DISTANCES (Å) CALCULATED FOR THE P-CYMENE CLATHRATE WITH RESPECT TO ONE HOST MOLECULE

PROTON	ORIENTATION A	ORIENTATION B	AVERAGED PROTON DISTANCES
H - 91	5,37		5,71[x]
H - 92	4,97		
H - 94	7,97		
H - 95	8,16		
H - 901	6,75		6,86[y]
H - 931	6,99		
H - 902a	9,15		6,63[z]
H - 902b	8,42		
H - 902c	8,99		
H - 903a	5,92		
H - 903b	7,36		
H - 903c	7,61		
H - 932a		6,27	
H - 932b		5,01	
H - 932c		6,69	
H - 933a		7,96	
H - 933b		8,76	
H - 933c		8,41	

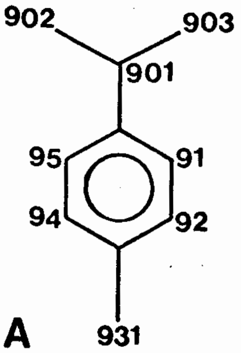
[x] Averaged distances for the C91, C92, C94 and C95 protons

[y] Averaged distances for the C901 and C931 protons

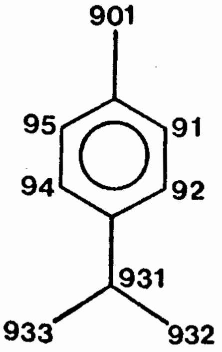
[z] Averaged distances for the C902, C903, C932 and C933 protons

The averaged proton distances were calculated using the equation,

$$r = \left[\left(\sum_{i=1}^{n} 1/r_i^{6}\right)/n\right]^{-1/6}$$



A



B

the benzene and the p-cymene guest molecules are similarly positioned with respect to the host molecules in solution. This is once again in accordance with crystallographic studies which indicate that the benzene and p-cymene molecules occupy the same centrosymmetric cavity in the tetragonal β-phase clathrate lattice.

5.4 EXPERIMENTAL

The benzene used was of Analar purity and the p-cymene was steam-distilled. The $Ni(NCS)_2(4\text{-}MePy)_4$ complex was synthesised as in Section 3.1. 400mg of the nickel complex dissolved in 1ml of deuterated chloroform (*i.e.* 0,73M) provided the metal-ion source. The titrations involved adding small volumes of the guest (benzene or p-cymene) to the host complex with a micro-syringe. Solutions were freshly prepared before use.

The spectra were recorded on a Brücker WH-90 spectrometer operating at 90MHz. Samples were allowed to equilibrate for 10min before spectra were recorded.

The longitudinal relaxation times (T_1's) were determined employing a Carr-Purcell $180^o - \tau - 90^o$ pulse sequence. The association constant K, was calculated by a least squares iterative simulation computed on a Univac 1106 computer with a specially written ASCII Fortran program.

CHAPTER 6

CHAPTER 6

DISCUSSION

The $Ni(NCS)_2(4\text{-}MePy)_4$ complex has great "clathrate"-forming ability thus giving rise to a variety of crystalline structures, the symmetry of which may vary from triclinic to hexagonal.

The Werner clathrates known to date may be simply classified in terms of molecular packing. (Refer to Table 6.1)

The tetragonal ($I4_1/a$) β-phase clathrate is the most well studied structure.

In the presence of an aromatic hydrocarbon, the non-clathrate α-phase $Ni(NCS)_2(4\text{-}MePy)_4$ complex of C_1 symmetry is transformed into a stable β-phase clathrate of C_2 symmetry. All the β-phase clathrate structures listed in Table 6.1 have their pyridine ligands in a "windmill" conformation. The torsion angles of the two symmetrically independent 4-methylpyridine ligands of all the β-phase clathrates, fall within a narrow range; $\tau_1 = \tau_4 = 32 - 35^{\circ}$ and $\tau_2 = \tau_3 = 41 - 44^{\circ}$[61]. Thus the conformation of the host molecules in the β-phase of the $Ni(NCS)_2(4\text{-}MePy)_4$ complex is almost completely independent of the guest component.

Furthermore, the void space between the β-phase host molecules is rather complex consisting of a three-dimensional set of cavities interconnected by means of channels. The various guest molecules all occupy the same centrosymmetric cavity. Non-centrosymmetric guest molecules such as m-xylene and p-cymene maintain the overall symmetry by means of disorder. In addition, the small methanol molecules (which suprisingly form a β-phase

TABLE 6.1 THE STOICHEIOMETRY AND LATTICE PARAMETERS OF THE Ni(NCS)$_2$(4-MePy)$_4$ CLATHRATES

Type of Packing	Guest Compound	Guest to Host Molar ratio[a]	Crystal Data
Channel			Tetragonal ($I4_1/a$)
	Benzene	1,05 : 1	$a = b =$ 17,02; $c =$ 23,18Å
	Toluene	0,90 : 1	——
	p-Xylene	0,88 : 1	$a = b =$ 16,98; $c =$ 23,62Å
	p-Cymene	0,77 : 1	$a = b =$ 17,105; $c =$ 23,84Å
	4-Me-Pyridine	1 : 1	$a = b =$ 17,09; $c =$ 23,44Å
	p-Dichlorobenzene	1 : 1	$a = b =$ 17,30; $c =$ 22,68Å
	Methanol	1,83 : 1	$a = b =$ 16,99; $c =$ 22,29Å
	p-, m-, o- Dinitrobenzene	1 : 1	——
	m-Xylene	1 : 1	$a = b =$ 17,28; $c =$ 28,87Å
Layer			Monoclinic and Triclinic
	Naphthalene	2 : 1	Cc $a =$ 16,27; $b =$ 16,46; $c =$ 31,93 Å $\beta =$ 89,3°
	1-Me-Naphthalene	1,51 : 1	$P2_1/c$ $a =$ 11,53; $b =$ 11,89; $c =$ 32,85 Å $\beta =$ 94,3°
	2-Me-Naphthalene	1,73 : 1	$P\bar{1}$ $a =$ 11,31; $b =$ 9,58; $c =$ 11,66 Å $\alpha =$ 115,5°; $\beta =$ 82,0°; $\gamma =$ 108,7°
	1-Br-Naphthalene	2 : 1	$P2_1/c$ ——
	2-Br-Naphthalene	2 : 1	$P\bar{1}$ $a =$ 11,31; $b =$ 9,54; $c =$ 11,76 Å $\alpha =$ 115,9°; $\beta =$ 81,7°; $\gamma =$ 109,6°
	o-Xylene	2 : 1	$P2_1/c$ $a =$ 11,48; $b =$ 11,49; $c =$ 32,72 Å $\beta =$ 96,6°;

TABLE 6.1 CONT/....

TABLE 6.1 CONTINUED

	p-Terphenyl	1 : 1	$P\bar{1}$	a = 11,25; b = 9,56; c = 10,73 Å; α = 83,3°; β = 80,7°; γ = 63,2°
	Bromobenzene	2,02 : 1	P_{nma}	a = 16,51; b = 15,74; c = 15,64 Å
Cage				
	p-Nitrotoluene	0,60 : 1	Hexagonal[b]	$a = b$ = 27,63; c = 11,16Å
	m-Nitrotoluene	0,60 : 1		$a = b$ = 27,98; c = 11,09Å
	o-Nitrotoluene	0,60 : 1		$a = b$ = 27,70; c = 11,21Å
	m-Br-nitrobenzene	0,66 : 1	$R\bar{3}$(?)	——
	o-Br-nitrobenzene	——	R(?)	$a = b$ = 55,26; c = 11,08Å
	Chloronitrobenzene	——	——	

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[a] The values given are the maximum guest content in the clathrate

[b] The space group has not been given in the reference

clathrate) are positioned within the centrosymmetric cavity in pairs, without methonal - methonal hydrogen bonding[61].

The dimensions of the cavities and channels are however greatly dependent on the molecular shape and concentration of the guest component. The lattice parameters for the benzene clathrate, $a = b = 17{,}02$Å and $c = 23{,}18$Å increase to $a = b = 17{,}105$Å and $c = 23{,}84$Å when substituting the more bulky p-cymene guest. The β-phase host lattice thus has the ability to dilate and contract in order to "mould" a guest species in its cavity. Lipkowski and Majchrzak[62] have prepared a series of $Ni(NCS)_2(4\text{-}MePy)_4 \cdot y$ 4-methylpyridine clathrate structures with guest to host molar ratios ranging from $y = 0$ to $y = 1{,}0$. Their results clearly indicate systematic increase in lattice parameters with increasing sorption of the guest species. They report that the dilation reaches as much as 10% of the total volume of the crystals.

The β-phase clathrate has a zeolitic-type structure rather than the typical clathrate one. The host framework is stable (or in the thermodynamic sense, metastable) for several days even in the absence of any guest.

During desorption of the guest, the volume of the clathrate crystals(*i.e.* the axial ratio c/a) is dramatically changed, hence the cracking of crystals may be observed.

Lipkowski has proposed two mechanisms[57] for the desorption process from the β-phase clathrate, based on the geometric fit between the guest molecules and the host cavities. The rate determining step for the p-xylene desorption from its 1 : 1 clathrate with the $Ni(NCS)_2(4\text{-}MePy)_4$ complex, is the breaking of the guest - cavity "bindings", *i.e.* release of the guest from its "cage". However when the guest molecule is far bulkier, then the barrier to diffusion becomes greater than the energy necessary to break the guest - cavity "bindings". Diffusion through the channel structure is thus the rate determining step for guest species such as meta- and ortho-dinitrobenzenes.

Clathrates with crystalline structure qualitatively different from the tetragonal, $I4_1/a$ lattice are called γ-modifications. These structures, having relatively high guest to host molar ratios are of layer-like type. The monoclinic γ-clathrates have asymmetric host molecules in "windmill" conformation whereas the γ-clathrates of triclinic symmetry have centrosymmetric conformations.

In these γ-clathrates, a variety of guest molecules occupy void space between closely-packed layers of the host molecules. The void space is sub-divided into cavities by virtue of protruding isothiocyanate ligands. The cavities have centres of symmetry each being occupied by two symmetrically located non-centrosymmetric guest species such as 2-Bromonaphthalene or 2-Methylnaphthalene. However a single centrosymmetric p-terphenyl molecule may occupy the cavity. Substitution of the p-terphenyl molecule by two centrosymmetrically located 2-Methyl- or 2-Bromonaphthalene molecules leads to host lattice dilation of $\sim 60 Å^3$ per unit cell[63]. The dilation is seen to result in a $\sim 0{,}5 Å$ lengthening of the *a* and *c* axes.

The γ-compounds are generally of lower stability than the β-clathrates. Furthermore the relatively "open" layer-like packing permits easy desorption of the guest. Crystals of 1- or 2-Methylnaphthalene lose guest components within minutes when placed in n-hexane (which does not dissolve the host structure). The o-xylene clathrate decomposes quickly in air at room temperature. Within a few minutes the crystals become opaque because of surface structure collapse[57].

Lewartowska and coworkers[54] have investigated the clathration of nitrotoluene isomers by the $Ni(NCS)_2(4\text{-}MePy)_4$ complex. The results of their X-ray powder diffractogram show that the crystalline structure of these nitrotoluene clathrates differs from that of the layer, γ-type and the channel β-type structures. The $Ni(NCS)_2(4\text{-}MePy)_4$.nitrotoluene clathrates crystallise in the hexagonal system. Furthermore their guest to host molar ratios are of the order of 0,6, whereas the maximum guest to host molar ratios of the β- and γ-clathrates equal 1 and 2 respectively. Desorption of the nitrotoluene isomers does not occur readily. These clathrates maintain a constant composition in air for more than a week. The crystals do not crack nor do they become opaque. This unusually high stability suggests a "true cage" structure. In contrast to the β- and γ-type structures, these cage-type clathrates are unselective towards para- and ortho-isomers.

A "true cage" structure has also been predicted for the enclathration of chloronitrobenzene and bromonitrobenzene by the $Ni(NCS)_2(4\text{-}MePy)_4$ complex[57].

Only Werner complexes of the type MX_2A_4 (where M = Ni, Co, Fe, Mn, Cu, Zn; X = NCS, CNO, NO_2; A = pyridine base, α-alkylarylamine, ester or amide of nicotinic acid etc.) have been reported to have potential clathrating ability. However the clathrate, PYRID, discussed in this work is of the type $MX_2A_2B_2$ (where M = Ni; X = NCS; A = 4-methylpyridine; B = 4-phenylpyridine). It would thus appear that host complexes other than the traditional MX_2A_4 type are able to form clathrates.

PYRID crystallises in the monoclinic space group and the pyridine ligands take on a "windmill" conformation. Continuous channels of void space between layers of host molecules are further sub-divided into cavities by the conformations of the pyridine and isothiocyanate ligands. The aliphatic guest molecule, methyl cellosolve, maintains the symmetry of the centrosymmetric cavity by means of disorder. Desorption of the methyl cellosolve molecules is usually observed, the crystals become opaque. The PYRID clathrate structure thus has properties of both the γ-phase layer-type and the β-phase channel-type structures.

A common feature of all the Werner clathrates known to date is their mode of guest-host interaction. Covalent bonds between the guest and host do not appear to exist. Further evidence as to the absence of specific chemical guest-host bonds has been obtained from our ^{1}H N.M.R. study of the p-cymene and benzene clathrates in solution. As mentioned previously, steric interactions alone are responsible for holding the guest species "captive" in their respective cavities. The results of our potential energy study of the PYRID clathrate structure is in accordance with this proposal.

De Radzitzky and Hanotier[37] have described a new family of Werner complexes displaying selective clathrating ability. Substituting the 4-methylpyridine ligands of the traditional Werner complex by primary substituted benzylamines, produces a host of new clathrate material.

These new Werner complexes only clathrate guest species containing at least one aromatic ring. Cyclic compounds derived from cyclohexane or decalin, cannot be enclathrated. They propose that the selectivity is related to both the electronic and steric nature of the amine.

A selectivity rule based on electronic factors alone may be formulated for the clathration of xylenes by complexes containing substituted α-methylbenzylamines. They propose that complexes in which the amine has on the para- or meta-position a substituent giving a negative inducing effect (F, Cl, I, Br) display para-selectivity. Whereas, when the subsituent gives a positive inducing effect (CH_3, C_2H_5 etc.) the complex displays an ortho-selectivity.

Steric factors however do play an important role, especially in the clathrating selectivity. The clathrated compounds must fit tightly in the voids of the crystalline lattice in order to give maximum cohesion with the aid of van der Waal's forces.

In contrast to the 4-methylpyridine Werner complexes, the substituted benzylamine complexes are not able to form clathrates by simple contact with the guest species. Clathration takes place only when the complex is allowed to crystallise in the presence of the potential guest.

Preliminary X-ray studies have shown that these new Werner complexes and their clathrates have a variety of crystalline forms. However in many cases conflict exists between steric and electronic factors making selectivities hard to foresee. Further experimentation is necessary in order to elucidate the clathration mechanism and to predict a priori which complex is able to perform a specific separation.

Researchers are thus striving to produce clathrate material with selec=tivities such that almost any desired aromatic isomer may be effectively separated. One clathration stage is often as efficient as a distillation in a column with hundreds of theoretical plates[37].

APPENDIX 1

OBSERVED AND CALCULATED STRUCTURE FACTORS

FOR PYRID

H	K	L	FO	FC
2	0	0	301	301
4	0	0	142	126
6	0	0	44	54
8	0	0	102	102
10	0	0	59	52
3	1	0	48	-56
5	1	0	18	-26
9	1	0	31	27
11	1	0	25	25
2	2	0	87	90
6	2	0	17	16
8	2	0	11	-4
1	3	0	108	-115
3	3	0	199	-195
5	3	0	103	-113
7	3	0	21	-29
9	3	0	17	-24
11	3	0	40	-44
0	4	0	103	-153
2	4	0	59	65
8	4	0	14	-7
1	5	0	108	77
3	5	0	16	18
5	5	0	18	12
9	5	0	19	21
11	5	0	21	23
0	6	0	502	507
2	6	0	47	-24
6	6	0	19	-13
8	6	0	41	43
10	6	0	17	16
1	7	0	64	57
3	7	0	41	50
0	8	0	197	-267
2	8	0	17	19
4	8	0	48	-44
6	8	0	19	-21
8	8	0	31	-34
10	8	0	13	-17
1	9	0	66	-97
3	9	0	77	-73
5	9	0	60	-59
7	9	0	20	-19
9	9	0	17	-21
0	10	0	84	-121
2	10	0	13	-16
4	10	0	9	-12
8	10	0	16	-16
1	11	0	99	84
3	11	0	75	75
5	11	0	66	62
7	11	0	26	24
9	11	0	13	16
0	12	0	118	159
2	12	0	30	-21
4	12	0	42	40
6	12	0	39	34
8	12	0	43	43
10	12	0	13	16
3	13	0	19	20
5	13	0	23	9
0	14	0	86	-108
2	14	0	16	-3
4	14	0	46	-47
6	14	0	43	-40
8	14	0	43	-40
1	15	0	31	-49
3	15	0	45	-45
5	15	0	41	-36
7	15	0	16	-13
0	16	0	12	-15
2	16	0	11	-5
4	16	0	11	-7
1	17	0	47	48
3	17	0	27	22
5	17	0	18	18
0	18	0	59	80
4	18	0	26	28
6	18	0	28	24
8	18	0	30	30
1	19	0	15	-4
3	19	0	11	-3
0	20	0	39	-39
4	20	0	26	-29
6	20	0	23	-24
1	21	0	15	-22
3	21	0	15	-21
5	21	0	20	-21
0	22	0	19	8
2	22	0	10	6
1	23	0	31	37
3	23	0	18	19
0	24	0	20	29
-11	1	1	13	-17
-9	1	1	44	-43
-7	1	1	30	-27
-5	1	1	33	-32
-3	1	1	162	-165
3	1	1	16	-6
5	1	1	154	-147
7	1	1	36	-39
11	1	1	33	-31
-8	2	1	55	-54
-6	2	1	90	-94
-4	2	1	20	15
-2	2	1	163	133
2	2	1	83	-54
4	2	1	119	-108
6	2	1	17	-19
8	2	1	45	-50
10	2	1	40	-40
-5	3	1	16	20
-3	3	1	43	32
-1	3	1	12	-27
1	3	1	46	61
3	3	1	10	18
5	3	1	23	21
-8	4	1	63	60
-6	4	1	100	104
-4	4	1	44	41
-2	4	1	174	-191
0	4	1	119	127
2	4	1	78	101
4	4	1	126	115
6	4	1	41	41
8	4	1	46	50
10	4	1	44	43
-9	5	1	25	28
-7	5	1	15	17
-5	5	1	25	28
-3	5	1	113	94
-1	5	1	46	21
1	5	1	168	189
3	5	1	23	27
5	5	1	132	123
7	5	1	29	29
9	5	1	11	-12
11	5	1	23	22
-10	6	1	10	-7
-8	6	1	13	-8
-2	6	1	12	-11
0	6	1	58	-53
2	6	1	32	39
-11	7	1	16	-19
-9	7	1	41	-40
-7	7	1	27	-23
-3	7	1	79	-85
-1	7	1	114	-103
1	7	1	116	-123
5	7	1	103	-99
7	7	1	32	-30
11	7	1	27	-29
-8	8	1	37	-34
-6	8	1	54	-53
-2	8	1	14	12
0	8	1	137	-136
2	8	1	98	-91
4	8	1	57	-54
8	8	1	27	-26
10	8	1	28	-28
-9	9	1	10	11
-7	9	1	16	13
-5	9	1	12	6
-1	9	1	18	18
1	9	1	36	34
5	9	1	25	19
7	9	1	12	7
-10	10	1	19	20
-8	10	1	60	58
-6	10	1	82	80

H	K	L	FO	FC
-4	10	1	71	59
-2	10	1	81	58
0	10	1	287	284
2	10	1	166	160
4	10	1	100	101
6	10	1	35	32
8	10	1	43	43
10	10	1	45	43
-9	11	1	31	34
-7	11	1	16	18
-3	11	1	13	9
-1	11	1	66	60
1	11	1	68	86
5	11	1	44	47
7	11	1	28	24
-6	12	1	16	-13
-4	12	1	25	-31
0	12	1	27	-36
4	12	1	22	-19
6	12	1	9	-6
-9	13	1	32	-34
-7	13	1	33	-32
-5	13	1	37	-32
-3	13	1	59	-56
-1	13	1	73	-57
1	13	1	71	-92
3	13	1	60	-53
5	13	1	88	-90
7	13	1	37	-35
-8	14	1	14	-10
-6	14	1	25	-23
-4	14	1	19	-15
0	14	1	38	-44
2	14	1	31	-48
4	14	1	28	-35
-9	15	1	22	20
-5	15	1	14	-11
-3	15	1	17	-9
-1	15	1	23	23
1	15	1	29	27
5	15	1	10	5
7	15	1	10	12
-8	16	1	14	15
-4	16	1	15	-13
-2	16	1	19	11
0	16	1	103	107
2	16	1	45	40
6	16	1	27	-21
-5	17	1	20	-19
-1	17	1	24	24
1	17	1	19	32
3	17	1	17	-4
-6	18	1	19	-17
-4	18	1	21	-31
-2	18	1	17	-19
0	18	1	32	-43
2	18	1	24	-17
4	18	1	30	-26
-7	19	1	21	-23
-5	19	1	25	-21
-3	19	1	22	-21
-1	19	1	43	-32
1	19	1	32	-39
3	19	1	38	-33
5	19	1	38	-43
7	19	1	19	-22
0	20	1	10	-12
-1	21	1	18	21
1	21	1	17	22
3	21	1	12	12
5	21	1	12	16
-4	22	1	19	20
-2	22	1	30	26
0	22	1	58	59
2	22	1	39	34
4	22	1	24	25
0	24	1	20	-27
-1	25	1	20	-20
1	25	1	18	-18
-10	0	2	36	-38
-8	0	2	73	-74
-6	0	2	129	-127
-4	0	2	166	-167
-2	0	2	320	-308
2	0	2	480	-478
4	0	2	165	-175
6	0	2	68	-63
8	0	2	22	-20
10	0	2	76	-71
-11	1	2	15	-15
-9	1	2	50	-49
-7	1	2	40	-37
-5	1	2	64	54
-3	1	2	133	118
-1	1	2	21	-21
1	1	2	34	-38
3	1	2	32	24
5	1	2	13	-10
7	1	2	41	-39
9	1	2	22	-21
11	1	2	13	-13
-6	2	2	45	41
-4	2	2	56	47
-2	2	2	11	11
2	2	2	78	65
4	2	2	77	58
8	2	2	30	-32
10	2	2	15	14
-11	3	2	15	20
-9	3	2	56	60
-7	3	2	78	73
-5	3	2	25	17
-3	3	2	81	-70
-1	3	2	208	192
1	3	2	182	163
3	3	2	102	93
5	3	2	160	142
7	3	2	79	80
9	3	2	12	11
11	3	2	23	22
-6	4	2	38	28
-4	4	2	40	35
-2	4	2	17	10
0	4	2	43	-85
2	4	2	84	77
4	4	2	67	42
6	4	2	14	10
8	4	2	20	-19
10	4	2	11	12
-9	5	2	44	-42
-7	5	2	37	-38
-5	5	2	38	32
-3	5	2	65	71
-1	5	2	48	-52
1	5	2	68	-76
3	5	2	18	17
5	5	2	35	-39
7	5	2	34	-38
9	5	2	15	-13
-8	6	2	21	-17
-6	6	2	40	-44
-2	6	2	13	18
0	6	2	111	80
2	6	2	119	-102
4	6	2	47	-55
8	6	2	20	20
10	6	2	35	-33
-9	7	2	12	-11
-7	7	2	18	-16
-5	7	2	12	1
-3	7	2	53	49
-1	7	2	54	-58
1	7	2	43	29
7	7	2	21	-20
-8	8	2	24	24
-6	8	2	53	50
-4	8	2	37	41
-2	8	2	44	51
0	8	2	54	20
2	8	2	97	105
4	8	2	71	76
6	8	2	30	24
10	8	2	25	25
-9	9	2	43	43
-7	9	2	61	57
-5	9	2	28	26
-3	9	2	12	13
-1	9	2	164	128
1	9	2	77	57
3	9	2	29	31

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
5	9	2	66	67	-8	14	2	31	32	2	18	2	38	-44	-4	2	3	27	29	-4	6	3	14	-18
7	9	2	54	56	-6	14	2	55	49	4	18	2	37	-36	-2	2	3	81	60	-2	6	3	9	-5
9	9	2	16	16	-4	14	2	35	28	6	18	2	29	-32	0	2	3	124	-106	0	6	3	13	-7
-6	10	2	20	16	-2	14	2	24	26	-6	20	2	30	29	2	2	3	61	-36	2	6	3	51	46
-4	10	2	16	18	0	14	2	25	22	-4	20	2	19	13	4	2	3	102	108	6	6	3	12	11
-2	10	2	32	23	2	14	2	52	59	0	20	2	10	11	6	2	3	101	99	-9	7	3	33	29
0	10	2	11	-30	4	14	2	77	71	2	20	2	26	27	10	2	3	16	16	-7	7	3	71	70
2	10	2	49	51	6	14	2	47	46	4	20	2	44	41	-5	3	3	17	-20	-5	7	3	59	61
4	10	2	34	22	8	14	2	16	17	6	20	2	29	28	-3	3	3	19	-26	-3	7	3	19	-21
6	10	2	16	16	-9	15	2	11	15	-5	21	2	25	22	-1	3	3	15	-16	-1	7	3	88	83
-9	11	2	30	-30	-7	15	2	33	32	-3	21	2	14	11	1	3	3	17	20	1	7	3	93	87
-7	11	2	48	-45	-5	15	2	43	38	-1	21	2	29	30	3	3	3	21	-11	3	7	3	66	56
-5	11	2	42	-40	-3	15	2	30	21	1	21	2	10	8	5	3	3	10	-18	7	7	3	30	32
-3	11	2	51	-42	-1	15	2	86	71	3	21	2	19	24	7	3	3	11	0	9	7	3	36	34
-1	11	2	93	-96	1	15	2	24	19	5	21	2	15	18	-10	4	3	31	-30	-10	8	3	23	25
1	11	2	60	-82	3	15	2	27	24	0	22	2	11	-17	-8	4	3	35	-33	-8	8	3	20	20
3	11	2	26	-27	5	15	2	30	32	4	22	2	11	-9	-6	4	3	63	-57	-6	8	3	40	38
5	11	2	50	-58	7	15	2	24	26	-1	23	2	34	-36	-4	4	3	52	-54	-4	8	3	36	32
7	11	2	38	-37	-4	16	2	14	12	1	23	2	19	-31	-2	4	3	135	-146	-2	8	3	89	80
9	11	2	15	-12	-2	16	2	15	6	3	23	2	19	-21	0	4	3	152	146	0	8	3	12	-11
-8	12	2	29	-26	0	16	2	11	-22	-2	24	2	12	-12	2	4	3	15	9	2	8	3	20	22
-6	12	2	58	-56	2	16	2	9	7	-9	1	3	38	28	4	4	3	138	-146	4	8	3	84	75
-4	12	2	25	-28	-7	17	2	23	-21	-7	1	3	100	98	6	4	3	115	-116	6	8	3	56	53
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-1	5	17	30	29
1	5	17	18	16
-1	7	17	35	-37

APPENDIX 2

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR CYMEN

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	2	0	172	223	2	12	0	119	127	-4	18	0	25	25	6	7	1	31	22	10	11	1	45	44
-2	4	0	88	67	4	12	0	15	11	-2	18	0	33	35	-7	8	1	72	66	-7	12	1	27	19
0	4	0	114	136	6	12	0	87	97	0	18	0	17	17	-5	8	1	81	72	-5	12	1	25	24
2	4	0	415	427	8	12	0	137	148	2	18	0	40	44	-3	8	1	166	156	-3	12	1	14	15
4	4	0	20	17	10	12	0	79	75	4	18	0	49	51	-1	8	1	25	22	-1	12	1	48	47
-4	6	0	185	188	12	12	0	25	27	10	18	0	27	27	1	8	1	76	71	1	12	1	38	40
-2	6	0	167	159	-10	14	0	19	23	12	18	0	31	37	3	8	1	21	34	3	12	1	52	53
0	6	0	73	72	-8	14	0	26	25	-8	20	0	23	19	5	8	1	97	101	5	12	1	42	50
2	6	0	50	47	-6	14	0	20	22	-6	20	0	30	34	7	8	1	37	38	7	12	1	48	42
4	6	0	224	239	-4	14	0	118	123	-2	20	0	27	26	-8	9	1	15	11	9	12	1	23	21
6	6	0	103	91	-2	14	0	105	108	0	20	0	43	42	-6	9	1	14	12	-12	13	1	25	24
-6	8	0	138	138	0	14	0	71	72	2	20	0	30	32	-4	9	1	32	32	-8	13	1	43	38
-4	8	0	137	148	2	14	0	22	19	6	20	0	22	18	-2	9	1	46	51	-4	13	1	47	50
-2	8	0	16	12	4	14	0	50	47	8	20	0	24	25	0	9	1	30	26	-2	13	1	62	65
0	8	0	158	169	6	14	0	50	54	-2	3	1	48	70	2	9	1	38	43	2	13	1	54	54
2	8	0	74	57	8	14	0	50	49	2	3	1	390	389	4	9	1	71	73	6	13	1	65	67
4	8	0	107	104	10	14	0	31	33	-3	4	1	134	126	6	9	1	52	61	8	13	1	29	29
6	8	0	124	128	12	14	0	38	38	-1	4	1	109	94	-9	10	1	22	22	10	13	1	18	26
8	8	0	169	172	-12	16	0	24	25	1	4	1	118	122	-7	10	1	69	71	12	13	1	32	30
-8	10	0	54	59	-8	16	0	61	60	3	4	1	64	76	-5	10	1	22	10	-9	14	1	24	26
-6	10	0	153	151	-6	16	0	31	28	-4	5	1	13	6	-3	10	1	20	23	-5	14	1	21	8
-4	10	0	86	89	-4	16	0	47	45	-2	5	1	155	135	1	10	1	42	47	-1	14	1	58	60
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2	10	0	157	158	0	16	0	63	61	2	5	1	77	60	7	10	1	35	35	3	14	1	23	20
4	10	0	188	193	2	16	0	22	27	4	5	1	120	126	9	10	1	61	65	7	14	1	26	30
6	10	0	133	143	4	16	0	28	28	-5	6	1	109	112	-8	11	1	24	26	9	14	1	30	37
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0	12	0	116	131	-6	18	0	41	35	4	7	1	39	40	8	11	1	22	26	-7	16	1	22	22

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5	16	1	17	9	-3	7	2	44	53	1	11	2	93	106	-5	15	2	64	61	2	3	3	175	212
13	16	1	21	23	-1	7	2	14	14	3	11	2	64	66	-3	15	2	39	37	-3	4	3	45	23
-2	17	1	26	29	1	7	2	146	141	5	11	2	32	39	-1	15	2	16	15	-1	4	3	342	319
0	17	1	24	22	3	7	2	151	161	7	11	2	55	63	1	15	2	26	33	1	4	3	218	228
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12	17	1	24	17	7	7	2	101	96	11	11	2	38	43	9	15	2	47	49	-4	5	3	112	108
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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
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0	5	25	16	7
2	5	25	25	27
4	5	25	17	23
-3	6	25	20	22
-1	6	25	24	24
5	6	25	22	23
-4	7	25	16	17
0	7	25	20	15
4	7	25	26	24
-3	8	25	17	15
-8	9	25	21	9
-6	9	25	17	11
0	9	25	22	19
6	9	25	18	8
-2	11	25	20	22
1	1	26	19	23
2	2	26	17	10
1	3	26	20	16
3	3	26	23	26
0	4	26	18	18
-3	5	26	17	18
-1	5	26	18	20
3	5	26	19	23
5	5	26	24	21
-3	7	26	21	11
-1	7	26	22	23
1	7	26	21	24
3	7	26	16	18
-3	9	26	18	17
1	11	26	25	21
3	6	27	17	7
-5	8	27	19	12
1	8	27	21	16
0	0	28	44	53
0	2	28	31	29
2	2	28	17	18
2	4	28	21	19
3	5	28	21	6
-2	6	28	19	15
6	6	28	19	12
0	1	29	20	22

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