WERNER CLATHRATES
WITH POTENTIAL CHIRAL SELECTIVITY
: PRELIMINARY INVESTIGATIONS :

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by

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This work is dedicated to my parents

ABSTRACT

The structures of the Werner clathrate $Ni(NCS)_2$(α-phenylethylamine)$_4$, as host complex made from enantiomerically pure amine ligand and from the racemic mixture, aswell as its clathrate with *sec*-butylbenzene have been determined by x-ray diffraction.

$Ni(NCS)_2$((*R*)-α-phenylethylamine)$_2$((*S*)-α-phenylethylamine)$_2$: $Ni(NCS)_2$((*R*)-α-phenylethylamine)$_4$ is orthorhombic with a = 15.543(2), b = 15.300(4), c = 14.747(29)Å, Z = 4 and the space-group $P2_12_12$. The structure consists of two independent molecules which have their -NCS groups *cis*.

$Ni(NCS)_2$((*R*)-α-phenylethylamine)$_4$ is orthorhombic with a = 15.587(3), b = 15.151(3), c = 14.773(2)Å, Z = 4 and the space-group $P2_12_12$. The structure consists of two independent molecules with differing conformations, but both have their -NCS groups *cis*.

The clathrate $Ni(NCS)_2$((*R*)-α-phenylethylamine)$_2$((*S*)-α-phenylethylamine)$_2$:*sec*-butylbenzene is monoclinic with a = 10.716(10), b = 30.604(6), c = 13.685(29)Å, Z = 4 and the space-group C2/c. The host molecules have their -NCS groups *trans* and the guest molecule, which lies on a two-fold axis, is disordered.

The complex $Ni(NCS)_2$((*S*)-α-phenylethylamine)$_4$, when formed in the presence of *sec*-butylbenzene, is triclinic with a = 11.641(4), b= 11.697(4), c = 14.868(9)Å, α = 71.28(5)°, β = 71.74(4)°, γ = 84.61(3)°, Z = 2 and the space-group P1.

The structure consists of two independent molecules with their -NCS groups *trans*, but display a different packing to the orthorhombic host structures.

The host complexes and the clathrates were investigated by various physical techniques, including UV/visible spectroscopy, mass spectroscopy, nuclear magnetic resonance spectroscopy, infra-red spectroscopy and x-ray powder diffractometry.

An energy calculation of the *trans*-to-*cis* transformation of the nickel complex gave the energy barriers as 27 - 35kcal/mol through a 'gauche' conformation, and ≈19kcal/mol for the *cis*-to-*cis* transformation through an 'anti' eclipsed form.

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CHAPTER 1

INTRODUCTION

1.1 Werner Clathrates of the type $[Ni(NCS)_2(subst.pyridine)_4]$

Among the rapidly increasing number and variety of organic and inorganic inclusion compounds, the so-called Werner clathrates (named after Alfred Werner, a pioneer of coordination chemistry), have received considerable attention. The cavity-containing structures of octahedral $[Fe(CNCH_3)_6]Cl_2$[1] and the clathrates of $Ni(NH_3)(CN)_2$ with guests such as thiophene and benzene[2] were already known when the paper of Shaeffer *et al*[3] on some new Werner hosts attracted wide interest. The authors reported the preparation and behaviour of ML_4X_2-type complexes, where M is a transition metal, L a pyridine derivative and X usually thiocyanate. Separation of xylenes, cymenes, methylnaphthalenes and other isomeric compounds was achieved by clathration with these inorganic complexes.

To date the host complex which Shaeffer examined most thoroughly, $Ni(NCS)_2(4\text{-Mepy})_4$, remains the one most widely studied. Some of the known clathrate structures of this and closely related host complexes are listed in Table 1.1. Most clathrates of this kind are formed with aromatic guest compounds, but there are also some with aliphatics, and even rare gases can be enclathrated[4].

The host complexes of this kind are synthesized by the double decomposition of nickel chloride with thiocyanate

TABLE 1.1 CLATHRATES WITH HOST LATTICES OF THE TYPE $|Ni(NCS)_2(SUBST.PYRIDINE)_4|$ †

Host complex	*Guest compounds*
$Ni(NCS)_2(4\text{-}MePy)_4$	benzene; toluene; p-, m-xylene;
(channel-type)	p-cymene; 4-MePy; p-dichloroben-
	zene; methanol; nitroethane[45]
	p-, m-, o-dinitrobenzene;
(layer-type)	naphthalene; 1-, 2-Me-naphtha-
	lene; 1-, 2-Br-naphthalene;
	o-xylene; p-terphenyl; bromoben-
	zene;
(cage-type)	p-, m-, o-nitrotoluene; m-, o-Br-
	nitrobenzene; chloronitrobenzene
$Ni(NCS)_2(4\text{-}EtPy)_4$	CCl_3 (two different crystalline
	forms)[46]; p-, m-xylene
$Ni(NCS)_2(4\text{-}VinylPy)_4$	$CHCl_3$[46]; p-, o-xylene[46]; THF[46]
$Ni(NCS)_2(3\text{-}MePy)_4$	$CHCl_3$[47]
$Ni(NCS)_2(4\text{-}PhenylPy)_4$	$(CH_3)_2SO$[47]
$Ni(NCS)_2(4\text{-}MePy)_2(4\text{-}PhenylPy)_2$	methyl cellosolve ($CH_3OCH_2CH_2OH$)

†Where not indicated otherwise, these clathrates are summarised in Reference No.44.

salt, and subsequent addition of the aromatic ligand. Clathrates are usually obtained by crystallizing the host complex from a solution in the prospective guest compound, whereby the solution need not generally be heated to a temperature effecting a breakdown of the tetramine complex to a diamine complex [5].

Thermal dissociation of these complexes shows that they are relatively unstable[6]: decomposition of the tetra-4-MePy complex occurs between 110 and 130°C[7]. The guest compounds of some of the clathrates may be removed without dissociation of the Ni-complex[5,8], although this ability does not seem to be directly related to the type of clathrate formed: for example, *p*-xylene and *m*-xylene form channel complexes with $Ni(NCS)_2(4\text{-Mepy})_4$, but only the *m*-xylene can be 'desorbed'. Escape of the guest molecules from some channel or layer clathrates results in instability of the host crystalline framework, as a result of which the crystals crack or become non-transparent; on the other hand relatively high visual stability suggests the cage-type structures in other Werner clathrates[9].

The Ni-complexes of all the host structures and clathrates which are listed in Table I.I have non-linear isothiocyanate groups in *trans*-positions. Extensive rotation about the Ni-N bonds produces structures with the pyridines in a wide range of relative orientations. This variation of molecular shape enables the complexes to adjust and thus enclathrate molecules of different size, shape and polarity[10]. Layer, cage and channel complexes are formed by bringing the Ni-

complexes in contact with suitable guest compounds. In some cases more than one unique cavity is created in a clathrate of the same molecular packing[11].

The selectivity of enclathration by these complexes[3] aswell as the sorption on the β-phases[12] is thought to depend on the shape more than the volume of the potential guest molecule, and on the shape of the ligand. Specific chemical host-guest interactions such as charge-transfer processes have been ruled out as factors contributing to the sorption properties, since neither parallelism of aromatic guest molecule and aromatic host ligands, nor some shortening of intermolecular distances in these groups has been observed.

However, while intermolecular forces owing to π-donor - π-acceptor charge transfer processes are expected to be strongest between molecules with electron-deficient and electron-rich substituted aromatic rings, weak π-π interactions exist between molecules in crystals of pure benzene. As the forces of interaction of this kind are relatively weak (interplanar distances close to those of graphite, 3.4Å), little or no distortion of the bonds of the components in the complexed state can be expected[13]. Evidence has also been produced that in the case of π-donor - nitroaromatic acceptor systems charge-transfer is not strongly influenced by changes in the orientation of the components with respect to each other[14]. In clathrate complexes of the type discussed in this work, substituted-benzene guest molecules were competitively captured on a scale dependent on the effect the substituents have on the electron density of the aromatic rings[7].

Generally, enclathration seems to be ruled both by steric constraints aswell as some, albeit weak electronic interactions between the host and guest molecules. Electronic interaction in substituted-pyridine-type Werner clathrates is obviously extremely limited because good overlap of the pyridine rings and aromatic parts of the guest molecules is geometrically impossible; selective enclathration here seems almost entirely based on steric considerations.

1.2 Chiral Separation and Recognition

Since Louis Pasteur postulated in 1860, that optical activity (that is the rotation of plane polarized light by solutions of certain compounds as discovered by the French physicist Biot in 1815[15]) is caused by an asymmetric grouping of the atoms in a molecule, and that molecules of the same substance rotating the plane of polarized light in opposite directions are related to each other by their mirror images[16], the stereochemistry, absolute configuration, racemisation and resolution of optically active molecules has become an important chemical subject. Van't Hoff[17] and le Bel[18] related their concept of a tetrahedral carbon atom to the rotation of plane-polarized light, and a distinction between optical and geometric isomerism was soon realized. As many compounds occurringin plants and animals were found as pure enantiomers, the total synthesis of such compounds (unless from optically pure precursors) usually involves a resolution step, as ordinary synthetic procedures lead to racemic modifications. Methods of resolution and the processes of chiral recognition have therefore been widely studied.

The first resolution to have been achieved was brought about by the *mechanical separation of crystals* by Louis Pasteur in 1848[19]. If macroscopic, enantiomeric crystals which are visually distinct are formed from a racemic solution, they may be picked apart under a microscope in the manner of Pasteur. Alternately, the optical activity of a chip of each crystal may be determined, and the crystals sorted in this way[20]. Because this method of separation is limited in application, tedious and time consuming, it is rarely used. A more useful variation of mechanical separation is that of inoculation. Discovered by Gernez[21], it produces a greater yield of one enantiomer by seeding a saturated solution of a racemic mixture with a pure crystal of one of the enantiomers.

One of the frequently used methods of chiral separation is that of *resolution by the formation of diastereoisomers*. The racemic mixture of the compound to be resolved is allowed to interact with an enantiomerically pure material to give a derivative, which consists of two diastereoisomers: i.e.

$$(\pm)\text{-A} + (-)\text{-B} \rightarrow (+)\text{-A} : (-)\text{-B} \text{ and } (-)\text{-A} : (-)\text{-B}$$

The two diastereoisomers have different properties and can be separated by distillation, chromatographic separation or, usually, crystallization. This is because the crystal structure is particularly sensitive to minor variations in molecular architecture.

The resolving agent should readily form a complex with the substance to be resolved, which in turn should easily be broken up. This condition is generally met by salts, and acids and amines are therefore easily resolved. Other substances must often be transformed into an acid first. The

compound formed should be nicely crystalline, there must be an appreciable difference in the solubilities of the two diastereoisomers and no double salts should form. The resolving agent should be cheap and easily and quantitatively recoverable after completion of the resolution. Examples of resolving agents are basic alkaloids like brucine, strychnine and epledrine, (+)-10-camphorsulfonic- and (+)-tartaric acid. A useful basic resolving agent is α-phenylethylamine, $C_6H_5CH(NH_2)CH_3$. Resolution of the *dl*-form is achieved with (-)-malic acid[22], glutamic acid[23], or very much more cheaply, (+)-tartaric acid[24].

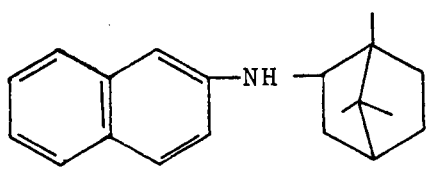
When the change of configuration at one chiral atom of a compound having two or more such asymmetric atoms establishes a physical or chemical equilibrium, and the asymmetric center which has changed may later be separated from the rest of the molecule, this provides a means of resolution, so-called *resolution by equilibrium asymmetric transformation*. Examples are the resolution of optically active 2-(*p*-carboxybenzyl)-1-hydrindanone and phenylchloroacetic acid[25]. This method, however, is only of limited general application.

Also of theoretical interest is the *resolution by kinetic asymmetric transformation*, which is the preferential formation, transformation or destruction of one or two or several diastereomers. The effect is caused by a difference in the free energy of different transition-state complexes of the reaction, which thus must constitute diastereomers and not just enantiomers.

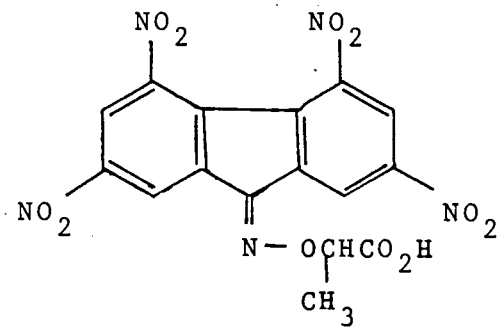
The production of optically active compounds by the inter-

vention of a living organism or by means of enzyme catalyst systems is termed *biochemical asymmetric transformation*, meaning that the interaction of the organism or enzyme with one enantiomer of a compound is faster than the interaction with the other enantiomer because of a difference in the free energy of activation for reaction[26].

Compounds lacking functional groups, such as saturated hydrocarbons, or possessing only weakly reactive functional groups, such as unsaturated aromatic hydrocarbons, ethers, alkyl halides and a variety of sulfonic compounds present a special problem in resolution, as they are unsuitable for resolution by the above methods. In some of these cases *resolution via molecular complexes* has been achieved. When a racemic mixture of a compound co-crystallizes with a dissymmetric reagent without formally reacting with it, the resulting two diastereoisomeric complexes have different solubilities, and one will precipitate in preference to the other. Decomposition of the precipitate will then yield one of the enantiomers of the original substance. (+)-2-Naphthylcamphylamine[27] and α-(2,4,5,7-tetranitrofluorenylideneamino-öxy)propionic acid[28] have been used as resolving agents in this manner. (Figure 1.1)



2-Naphthylcamphylamine



α-(2,4,5,7-Tetranitrofluorenylidene-aminoöxy)-propionic acid

Figure 1.1

1.3 Chiral Discrimination by Inclusion Compounds

H.M.Powell first suggested that dissymmetric cages formed by host molecules could provide a chiral environment around a trapped guest molecule and lead to preferential inclusion of one of the enantiomers of a racemic mixture of guest molecules[29].

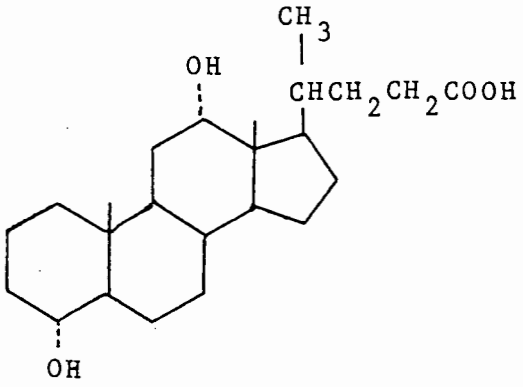
Choleic acids, which are the inclusion compounds of desoxycholic acid (Fig. 1.2), resolve camphor and partially resolve dipentene[30]. Stereospecific and regiospecific photoreactions inside the channels of choleic acids have also been described[31]. In these reactions, as in all enzyme-catalyzed reactions the proximity and preferred or even prescribed orientations between the host and the substrate or guest molecules enable selective reactions on the guest molecules.

Extensive studies have been carried out on the inclusion compounds formed by crown ethers. Chiral crown ethers with catalytically active groups in their periphery have been used as enantiospecific catalysts[32].

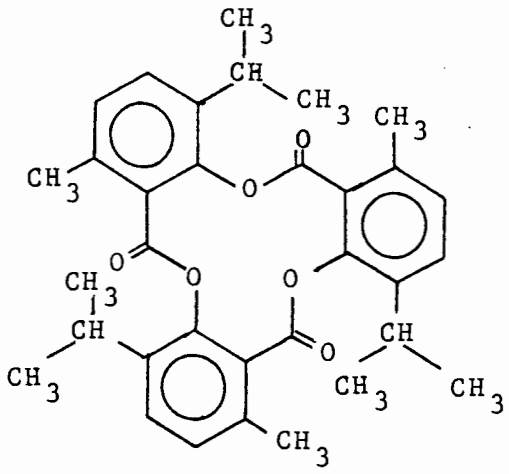
Urea crystallises in an asymmetric, spiral-shaped manner which, depending on which spiral is formed, will preferentially include one of the 2-chlorooctane enantiomers[26].

Cyclodextrin, which is a cyclic glucose oligomer, forms molecular inclusion compounds, and has been used to resolve ethyl mandelate, $C_6H_5CHOHCO_2C_2H_5$[33].

A clathrating compound which displays significant chiral recognition is tri-o-thymotide, TOT, $C_{30}H_{36}O_6$ (Fig. 1.2).



Desoxycholic acid



Tri-o-thymotide

Figure 1.2

TOT has already been shown to afford complexes with more than 100 different guest molecules. The stereoselective properties of TOT were first reported in 1980 by Arad-Yellin *et al*[34]. In solution the TOT-molecule exists primarily in a propeller-like chiral conformation, with rapid interconversion between the (P)- (right-handed) and (M)- (left-handed) forms taking place. The activation energy for this enantiomeric isomerisation process was reported as ≃21kcal/mol[35]. While the uncomplexed TOT crystallizes in the achiral space-group $Pna2_1$, with equal amounts of (P)- and (M)-forms present[36], it often undergoes spontaneous resolution upon crystallisation with guest molecules, even if these are achiral themselves[20]. Crystallisation from racemic chiral solvents which are suitable guest molecules, affords chiral single crystals (either (P)- or (M)-type TOT) with guest enantiomers incorporated to different degrees[34]. The stereoselectivity is measured as enantiomeric excess (%e.e.), and some examples are[37]:

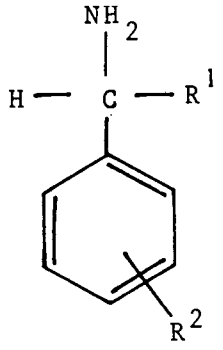
Guest molecule	2-butanol	2-amino-butane	2-chloro-butane	2-bromo-butane	ethyl-methyl-sulfoxide
% e.e.	<5	<2	45	35	40 - 50

In an attempt to explain the differences in stereoselectivity of TOT between, for example, 2-bromobutane and 2-butanol, Gerdil and Allemand[37] compared calculated minimum energies for the inclusion of enantiomeric molecules within a rigid cage of a given chirality. It was found that the (M)-TOT:(R)-2-bromobutane association was more favourable by ≃3.5kcal/mol than the (M)-TOT:(S)-2-bromobutane association. In the case of 2-butanol, for which an enantiomeric excess of 5% was recorded, packing calculations revealed that both enantiomers could be enclathrated by either (M)- or (P)-TOT at the expense of about the same energy. Arad-Yellin *et al*[20] found that guest molecules containing near of true 2-fold symmetry (the symmetry of the cage cavity) tend to afford higher enantiomeric purities, as coincidence of host cavity and guest molecule symmetry is possible, while molecules of C_1 symmetry, which must be disordered in the cage cavities, display widely varying enantiomeric guest purities.

In the enclathration of chiral guest molecules a remarkable correlation of the configuration among comparable guests was found: i.e. all (S)-guests of a given kind were preferentially enclathrated by the (P)-TOT. TOT-complexation was thus suggested as a way to assign configurations especially to guest molecules which lack functional groups generally required to achieve resolution by diastereomeric interactions.

1.4 Werner Complexes with Arylalkylamine Ligands

A new family of Werner complexes formed between nickel-isothiocyanate and substituted primary benzylamines, $[Ni(NCS)_2(R^2\text{-}C_6H_4\text{-}(CH\text{-}R^1)\text{-}NH_2)_4]$, was introduced in 1962 by de Radzitsky and Hanotier[7]. The amino compounds were of the following type:



with R^1 = Me, Et, Pr, *iso*-But, Am, Hex, Oct;

and R^2 = H, *p*-Me, *o*-Me, *p*-Et, *p*-Isoprop, *p*-*tert*-But, *p*-OCH_3, *p*-F, *p*-Cl, *p*-Br, *m*-Br, *p*-I, *m*-NO_2.

The Ni-complexes were shown to display significant clathrating ability for, and also selectivity among various xylenes and methyl-naphthalenes. The compounds enclathrated by the simplest of the Ni-complexes described, $[Ni(NCS)_2(\alpha\text{-phenylethylamine})_4]$ include propyl-, butyl-, ethyl-, n-heptyl-, ethylisopropyl-, trimethyl-, dimethylethyl- and dichlorobenzenes, xylenes, ethyl- and chlorotoluenes, cymenes, naphthalene and biphenyl. From this it was deduced that compounds to be enclathrated should contain at least one aromatic ring, and that accumulation of polar groups or bulky substituents makes a compound less easily enclathrated.

It was noted that $Ni(NCS)_2$ forms tetramine complexes with both pure (*d*)- or (*l*)-α-phenylethylamine, but that neither is able to form clathrates; a maximum clathrating capacity is reached when the racemic mixture is used.

Thermal dissociation of the α-phenylethylamine complex and its *o*-xylene clathrate shows that this nickel complex is even less stable than the nickel complexes with 4-MePy. It was suggested that the reason for this was the steric hindrance experienced by the nitrogen atoms in the α-arylalkylamine complex, which would prevent the lone pair of electrons of the N-atoms to come as close to the Ni-atom as in the case of the 4-alkylpyridine complexes. The *o*-xylene clathrate was completely dissociated to tetramine complex and free *o*-xylene at ≃60°C.

It was noted that in contrast to the 4-alkylpyridine complexes, the substituted benzylamine complexes do not form clathrates by mere contact with the prospective guest compound, but only if the formation of the tetramine complex takes place in the presence of the guest compound. Preliminary x-ray studies were reported to have shown that the host complexes and the clathrates have different crystalline forms.

Further studies in the Labofina laboratories[38] showed that the amine ligands must have an aromatic ring in the alpha position of the amino-group.Benzylamine, the first member of such a homologous series, is an exception as its tetramine complex with $Ni(NCS)_2$ does not possess clathrating abilities. Competitive enclathration of ten monosubstituted benzenic derivatives by $[Ni(NCS)_2(\alpha\text{-phenylethylamine})_4]$ resulted in the following selectivity scale: (only substituents of the benzene ring are named)

$$tert\text{-}C_4H_6 > CH_3 > iso\text{-}C_3H_7 > H > Br > OCH_3$$
$$> COOC_2H_5 > NO_2 > C_2H_5 > CF_3$$

It was deduced that electron-releasing substituents increase the clathration affinity of benzene derivatives, and *vice versa*. However, depending on the electron density of the aromatic ring of the amine ligand, the above selectivity scale can be reversed: for $[Ni(NCS)_2\{\alpha$-(3,4,5-trimethylphenyl)ethylamine$\}_4]$ it was found to be:

$$CF_3 > NO_2 > Br > CH_3$$

This was thought to indicate interactions of the charge-transfer type between the host and guest molecules of the clathrate. However, no evidence of such charge-transfer could be obtained from electronic spectra. If these processes do occur, they were thought not to have been detected because they are too weak and the bands fall in the far U.V. region. Infrared spectra of the clathrates, however, are very different from the sum of the spectra of the host and guest conformers, which could be interpreted in terms of charge-transfer interactions. However, later studies have shown that the observed spectral anomalies can be interpreted assuming steric interactions alone[39,40].

X-ray studies, which were never completed as Labofina abandoned this project[41], revealed that in the crystalline lattice of the α-arylalkylamine type complexes, the aromatic nuclei of amines of adjacent molecules are parallel to each other (Figure 1.3), and the aromatic rings of enclathrated molecules were expected to be positioned parallel between the aromatic ligands of the host, thus enabling electronic interactions to take place.

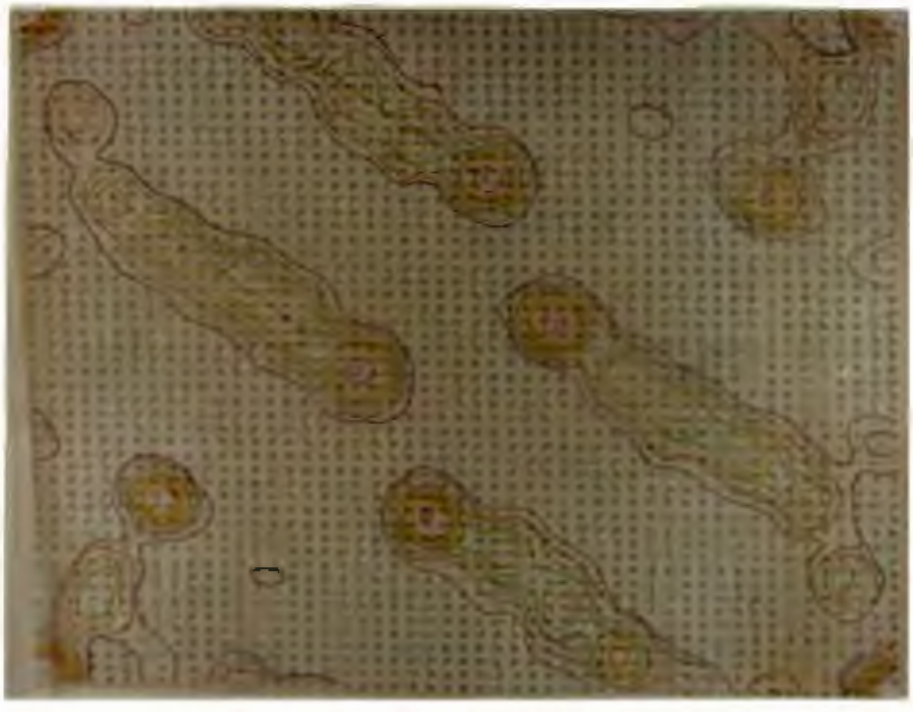


Figure 1.3 Fourier map in the *ab* plane of a $[Ni(NCS)_2(\alpha\text{-alkyl-4-chlorobenzylamine})_4]$[¶]

Other physical determinations[42] showed that there is a threshold concentration of guest molecules in an inert solvent, below which clathration by these complexes cannot take place. The process of clathration was shown to be truly reversible and exothermic during the formation of the clathrate. The compounds formed with the guest molecules appeared to be true stoichiometric compounds.

According to the following scheme (Fig. 1.4), clathrates of this type have been used at Labofina S.A. in a cyclic process to purify *m*-xylene from a mixture with *p*-xylene[43].

[¶]*courtesy of Dr A Leonard, Université Catholique de Louvain*

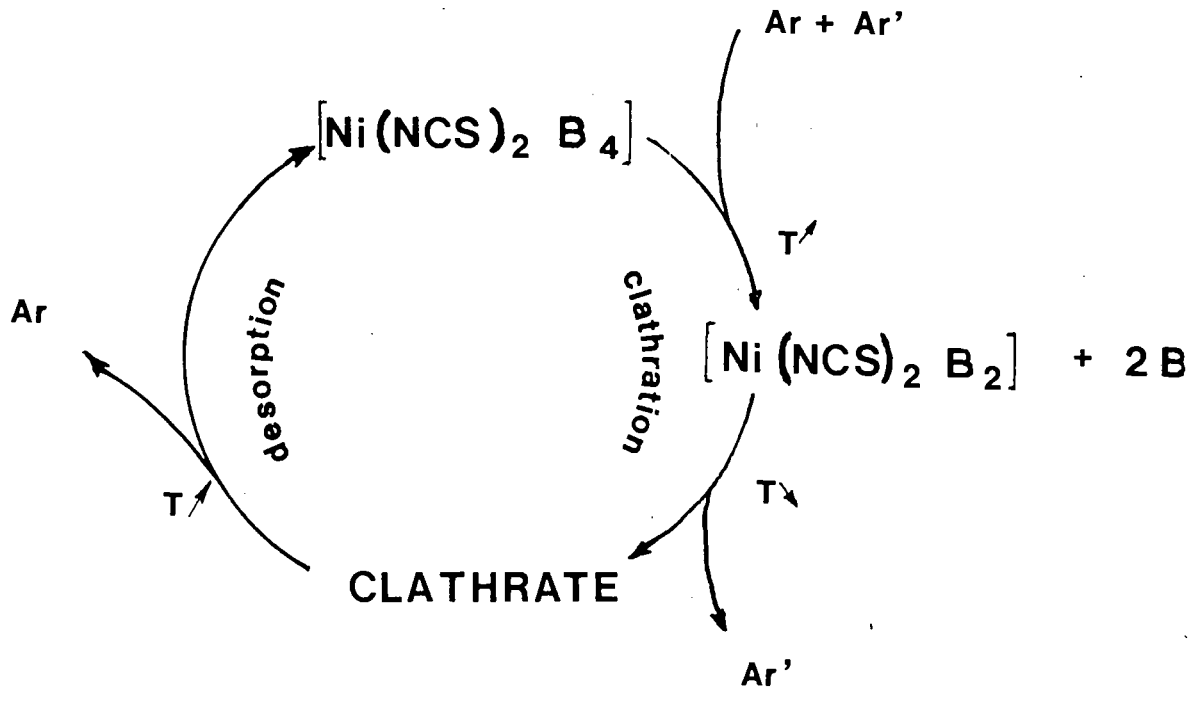


Figure 1.4 "Labofina S.A. clathration process"
B represents an α-arylalkylamine

1.5 Aims of the Present Study

Attempts to mimic the extraordinary high degree of chiral discrimination displayed by biological systems on interaction with racemic substrates have been carried out by many scientists, and the synthesis and resolution of chiral substances play an important rôle in contemporary synthetic chemistry.

The motivation for this work has been to investigate the features that control the process of clathration by nickel complexes which may be synthesized from chiral ligands. The nature of the most basic of the $[Ni(NCS)_2(\alpha\text{-arylalkylamine})_4]$ host complexes is studied with a view to obtaining clathrates of this general type displaying chiral selectivity for guest compounds. $[Ni(NCS)_2(\alpha\text{-phenylethylamine})_4]$ has been shown to enclathrate selectively geometric isomers of a wide

variety of hydrocarbons, some of which have chiral carbon atoms but lack the functional groups normally required to achieve resolution via diastereoisomerisation. Selective enclathration of enantiomers would therefore provide a useful method of resolution.

In contrast to the tri-o-thymotide molecule which does not exist in just one of two chiral forms, but often forms crystals in only one or the other chiral propeller-like conformations, the nature of the nickel complexes described here is such that ligands with known chirality may be used to form a host complex which consequently is inherently chiral. If, as a result, selective enclathration could be achieved, this could be used in a cyclic process without having to determine the chirality of each crystal, as is necessary with inclusion compounds of tri-o-thymotide.

The complex studied is nickel bis-isothiocyanate-tetra-alpha-phenylethylamine,, made from the racemic mixture of the chiral amine and from both pure (*d*)- and (*l*)-forms of the ligand. The pure (*d*)- and (*l*)-complexes were reported not to form clathrates, while the optically inactive complex yielded clathrates with a variety of guest compounds. This suggests that steric rather than kinetic factors control the clathration process, and that the final state, as observed by x-ray crystallography, may be used to explain some of the factors responsible for guest inclusion in these complexes. A greater understanding of these factors may lead to the synthesis of new host complexes with chiral selectivities towards guest complexes.

C H A P T E R 2

CHAPTER 2

EXPERIMENTAL

2.1 Preparation of Complexes[7]

2.1.1 The Host Complexes from (*d*)-, (*l*)- and (*dl*)-α-Phenylethylamine

The complexes were formed by dissolving $NiCl_2.6H_2O$ (1.43g, 0.006mole) and KSCN (1.17g, 0.012mole) in 6ml distilled water, yielding a solution of 0.006 mole of $Ni(NCS)_2$. To this was added slowly, with stirring, enantiomerically pure (*d*)- or (*l*)-, or a racemic mixture of α-phenylethylamine (3.25g, 0.027mole - a 12% excess). A blue precipitate formed immediately. When this had a syrup-like consistency, further stirring prompted crystallization. The precipitate was separated by filtration on a Büchi apparatus, washed twice with 5ml cold *n*-hexane, and dried under vacuum at room temperature.

2.1.2 The $[Ni(NCS)_2(\alpha\text{-phenylethylamine})_4]$ Complexes with *Sec*-Butylbenzene and *O*-Xylene

The following method was used in attempts to form clathrates with host complexes made from pure (*d*)-, (*l*)- and racemic α-phenylethylamine with *sec*-butylbenzene and also *o*-xylene as prospective guest compounds.

A solution of $Ni(NCS)_2$ (0.006mole) was prepared as above and cooled in an icebath. The amine ligand (3.25g, 0.027mole) was dissolved in ≃10ml of the prospective guest compounds.

This solution was then added dropwise while stirring, to the nickel isothiocyanate solution. The resulting blue precipitate was washed and filtered as above, and vacuum dried for only one hour.

2.2 Crystal Growth

2.2.1 Host Complexes

Single crystals for x-ray diffractometry were obtained by dissolving about 50mg of the Ni-complex in 2ml methanol. The colour of this solution is bluish-green, and does not resemble the typical blue of the $Ni(NCS)_2(subst.pyridine)_4$ solutions. Slow evaporation of the solvent from a vial yielded crystals on the walls of the vial , and as the complex concentration increased, crystals formed in the solution.

2.2.2 Host-Guest Complexes

Crystals of all the complexes prepared as in Section 2.1.2 above were obtained by dissolving about 50mg of a complex in 2ml methanol, and adding 0.5ml of the prospective guest compound, i.e. *sec*-butylbenzene or *o*-xylene. Small single crystals were obtained from within the solutions, as crystals from the walls of the vials above the solutions often were composed of only the host complex, even if clathrate crystals were found in the solution.

It should be noted here that the small quantity of clathrate complex, upon sufficient evaporation of methanol, was able to form a microcrystalline lattice of small, needle-

shaped crystals which caused even a large remaining volume of 'guest' solvent to set in its container. In addition, a transparent, plastic jelly-like substance repeatedly formed in the vials containing the *o*-xylene clathrate dissolved in methanol and some added *o*-xylene. The composition of this substance, however, was not further investigated.

2.3 Physical Methods

2.3.1 Microanalysis

Microanalysis was performed on the complexes to determine their carbon, hydrogen and nitrogen content. The method is based on Heraeus universal analyser, and carried out on a model CHN-MIKRO after Monar[48].

2.3.2 UV/Visible Spectroscopy

UV spectra of the complexes and clathrates were obtained to see whether, in solution, electronic interactions between host and guest molecules were detectable. Spectra of *n*-hexane solutions of the amine ligands with *sec*-butylbenzene at different relative concentrations showed no new peaks arising from electronic ligand-guest interactions (i.e. prior to complex formation). Spectra of the complexes were obtained on a Unicam SP1800 spectrophotometer using 1cm quartz cells.

2.3.3 Mass Spectroscopy

This technique has been described as a useful means of identifying the guest species in the clathrate structure[47]. The guest molecules, which are not chemically bonded to the

host network, were likely to be more readily volatilized than the host complex, and the total ion current spectrum revealed two distinct peaks for samples of the $[Ni(NCS)_2(4\text{-}MePy)_2(4\text{-}PhPy)_2]$ clathrate with methyl cellosolve[44], the $[Ni(NCS)_2(4\text{-}PhPy)_4]$ clathrate with DMSO and the $[Ni(NCS)_2(3\text{-}MePy)_4]$ clathrate with chloroform[47]. (See Fig. 2.1)

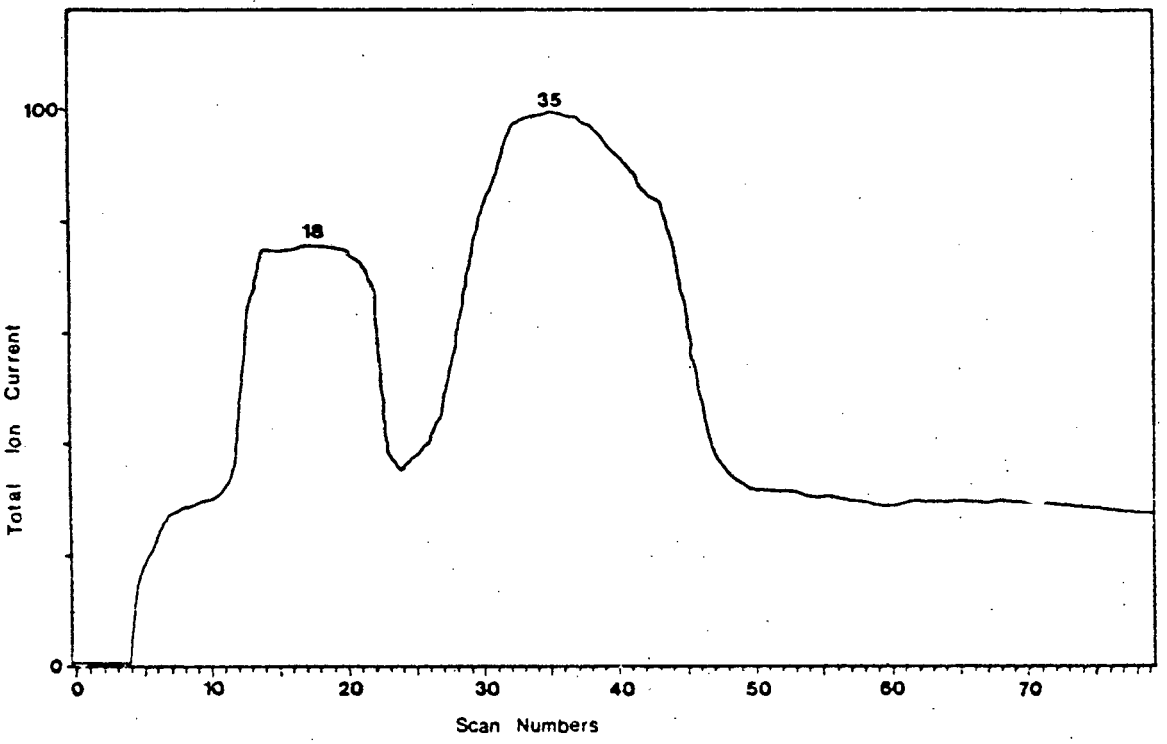


Figure 2.1 The total ion spectrum of $Ni(NCS)_2(4\text{-}PhPy)_4.4DMSO$ ¶

From fragmentation patterns it appeared that during scans of the first peak simultaneous breakdown of the host complex and guest molecules occurred, while at higher scan numbers the fragments observed were related to the host structure only.

Mass spectra of the complexes presented in this work were

¶ *courtesy of S.Papanicolaou*[47]

thus recorded in the hope of identifying the complexes as merely host structures or as host-guest clathrates. The spectra were recorded on a V.G.Micromass 16F Spectrometer operating under the following conditions:

Electron beam energy:	70 eV
Accelerating voltage:	4 kV
Source temperature:	170 - 200 ^{o}C

2.3.4 Gas Chromatography

The separation of isomers of some organic compounds by chromatographic means using nickel clathrate compounds was first reported by Kemula and Sybilska in 1960[49]. Isomeric nitrophenols, nitroanalines, chloronitrobenzenes and nitrotoluenes were successfully separated by nickel isothiocyanate complexes with β- and γ-picoline and 2,6-lutidine as stationary phases. Use of the $Ni(NCS)_2(\alpha\text{-arylalkylamine})_4$ complexes in GC was reported by Bhattacharyya *et al*[50]. Elution orders found for a column with 30% $Ni(NCS)_2(\alpha\text{-phenylethylamine})_4$ were:

A) Cyclohexane < cyclohexene < benzene

B) Methylcyclohexane < toluene

C) Benzene < toluene < chlorobenzene < (m+p)xylenes < o-xylene < 1,3,5-trimethylbenzene < 1,2,3-trimethylbenzene

D) n-Hexane < n-heptane < 2,2,4-trimethylpentane

for a column run at 30^{o}C (except 60^{o} for series C), N_2 as carrier gas and a flow rate of 30cm^3/min.. These results confirmed that the greater the electron density of the aromatic

ring in sterically comparable guests, the greater the interaction with the tetramine complex, and the larger the retention times of the guests. However, in a review of inclusion compounds in chromatography it was suggested that factors such as vapour pressure and diffusion do not allow the weak electronic effects to become sufficiently perceptible in these arylalkylamine complexes[51].

In this work columns were prepared with host complexes of enantiomerically pure, aswell as racemic α-phenylethylamine, in order to investigate whether any differences in retention could be observed for the chiral *sec*-butylbenzene and some other organic compounds.

Columns were made from 100cm glass tubes (4mm I.D.), and were packed with Chromosorb W coated with 30% (by weight) of the nickel complex, -80 to +100 mesh. A Pye Unicam PU4500 GC with F.I.D. was used, with N_2 as carrier gas. The dead volumes of the columns were calculated from the transit times of a 2µl sample of petrol, which was considered non-retained. The columns were cured at 70° under N_2 flow for several hours before analysis.

2.3.5 Nuclear Magnetic Resonance Spectroscopy

When it became apparent from structure determinations that the $Ni(NCS)_2(\alpha\text{-phenylethylamine})_4$ complex could exist in more than one stereoisomeric form, NMR spectra were obtained to determine whether, in solution, these isomeric forms were in equilibrium with each other.

It has been noted that a characteristic feature of the Ni(II)

chemistry is the low energy difference between different stereochemical forms, which often results in equilibria between various structural types occurring in solution. Such equilibria are the *octahedral-square planar*, where the square planar (diamagnetic) and octahedral (paramagnetic) complexes are interconvertible in the following manner:

$$NiL_4 + 2L' = trans\text{-}[NiL_4L'_2]$$

monomer-polymer and *tetrahedral-square planar equilibria*[52], and the intramolecular *cis-trans* rearrangement of the type $[Ni(\text{unidentate A})_2(\text{unidentate B})_4]$. Such *cis*-to-*trans*-to-*cis* isomerisation (of $[M(ER_3)_2(CO)_4]$) has been demonstrated by analysis of the ^{13}C-nmr lines indicative of ligand scrambling[53].

^1H resonances were determined in this work for host and guest complexes in deuterated methanol, using TMS as standard. The spectra were recorded on a Brucker WH90 (90MHz) NMR spectrometer.

(In the presence of a paramagnetic ion peak broadening effects caused by an improved efficiency in spin-spin relaxation processes are usually expected to occur. The Ni(II) ion, which is paramagnetic in octahedral configuration, can also shift the resonances rather than broadening them[44].)

2.3.6 Infra-Red Spectroscopy

Infrared spectra of the α-arylalkylamine clathrates were reported to be different from a superposition of the spectra of the host complexes and of the guest compounds[42,54]. From spectra of the xylene-clathrates of the $[Ni(NCS)_2(\alpha\text{-phenyl-}$

ethylamine)$_4$] complex and in the absence of other structural data, the following conclusions were drawn:

1) the thiocyanate groups were bound to the nickel through the nitrogen;
2) in the amine, the intensity of the asymmetric ν_{NH} vibration band is higher than that of the symmetric ν_{NH} band. The reverse is true in both host complexes and clathrates;
3) the band in the amine assigned to H-bonding disappears in both host complexes and clathrates;
4) in the spectra of the clathrates a band is found which disappears on storage of the clathrate.

When, during the course of this work, structural differences in the Ni-complexes of the host and clathrate structures respectively became apparent, infrared spectra were recorded in order to relate these differences to their respective absorption bands.

In the crystal structures the point group symmetry of the Ni-complexes in the host structures is C_2, and in the clathrate with *sec*-butylbenzene it is D_{2h}. By the application of group theory to the prediction of vibrational spectra[55] the number of νNi-NCS bands expected to be infra-red active were determined:

$\Gamma_{\nu Ni\text{-}NCS} = A + B$ for the C_2 *cis*-complex

$\Gamma_{\nu Ni\text{-}NCS} = B_{1u}$ for the D_{2h} *trans*-complex

The number of Ni-N bands for the amine ligands expected to be IR active are:

$\Gamma_{\nu Ni\text{-}N} = 2A + 2B$ for the C_2 *cis*-complex

$\Gamma_{\nu Ni\text{-}N} = B_{2u} + B_{3u}$ for the D_{2h} *trans*-complex

As the absorption band which was reported to disappear on storage of the clathrate falls in the region of ν_{NC-S} bands of some other nickel complexes[56], the expected number of IR active stretches were also determined:

$$\Gamma_{\nu NC-S} = A + B \quad \text{for the } C_2 \textit{ cis}\text{-complex}$$

$$\Gamma_{\nu NC-S} = B_{1u} \quad \text{for the } D_{2h} \textit{ trans}\text{-complex}$$

assuming that the isothiocyanate groups are linear. In the crystal structure of the clathrate with *sec*-butylbenzene, however, they are distorted from linearity, and if the general point-group D_{2h} is retained, contributions of three bands arise at least theoretically: $B_{1u} + B_{2u} + B_{3u}$. The site symmetry of the ligands here is lower than the molecular symmetry, and solid state splittings of nondegenerate vibrations can be expected. These may be determined by factor group analysis[57], an account of which lies beyond the scope of the present study.

IR spectra of the complexes and clathrates as Nujol mulls were obtained on a Perkin Elmer 983 IR Spectrometer, using CsI sample plates. The derivation of the number of IR active bands for the Ni-NCS, Ni-N (amine) and NC-S stretches is discussed in Appendix 2.

2.3.7 X-Ray Powder Diffractometry

In previous studies of inclusion phenomena, powder diffractograms have been utilized to determine the stability of clathrates and detect changes in the host lattice on desorption of guest molecules[42,47,58]. They also provide a fast method of distinguishing the unclathrated host structure

from a clathrate when these structures are different.

In this work diffractograms were obtained on a Philips automatic x-ray powder diffractometer PW1050/80, using CuK_α radiation. The samples were contained in aluminium sample containers, and operating conditions were as follows:

X-Ray Generator:	40kV
	20mA
Counter:	1000c/s
time constant:	2s
Scan speed:	2° 2θ/min

2.3.8 Single Crystal Diffractometry

Single crystals of the host complexes were unstable and had to be mounted in sealed Lindemann capillary tubes, into which some mother liquor was introduced. In some cases preliminary crystallographic information was obtained from oscillation and Weissenberg (zero- and upper-layer) photographs. These were taken using a Stöe goniometer and camera (r=28.65mm). Nickel-filtered CuK_α radiation (λ=1.5418Å) was generated by a Philips PW1120 x-ray generator operating at 20mA and 40kV.

Diffractometer data collections were obtained on an Enraf-Nonius CAD4-diffractometer, using graphite-monochromated MoK_α radiation (λ=0.71069Å) obtained from a Philips PW1730 generator. Accurate cell dimensions were determined by least squares analysis of typically 25 high order reflections. Data were corrected for Lorentz-polarization, and an empirical absorption correction was once applied[59]. To monitor instrumental stability and crystal degradation during the data

collection, three standard reference reflections were measured periodically.

All computations were performed on a Sperry 1100 main-frame computer at the University of Cape Town. The following programs were employed:

SHELX-76[60]: for crystallographic data reduction, structure solution and refinement. Features of the program which were used include data reduction, calculation of Patterson and difference Fourier maps, full-matrix and blocked full-matrix least-squares refinement. Hydrogen atoms (except those bonded to the nitrogen atoms) were geometrically positioned w.r.t. their parent carbons and allowed to ride, with U_{ij} free on the carbon atoms they were bonded to. The C-H bond distances were fixed to 1.00 Å in all cases. Unless otherwise specified, the temperature factors of hydrogens in tertiary -CH, primary $-CH_3$ and benzene-type -CH groups respectively were tied together. The only weighting scheme employed was $w=k/|\sigma^2 F|$. Where atoms on special positions were treated anisotropically, symmetry restrictions were applied according to Peterse and Palm[61].

The agreement between observed (F_o) and calculated (F_c) structure factors is expressed by the conventional residual R, defined as:

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

or as a weighted index:

$$R_w = \frac{\Sigma w^{\frac{1}{2}}|\Delta|}{\Sigma w^{\frac{1}{2}}|F_o|}$$

The generalized residual employed in the applications of Hamilton's test is calculated as follows:

$$R_G = \sqrt{\frac{\Sigma w|\Delta|^2}{\Sigma w|F_o|^2}}$$

The calculation of a goodness-of-fit parameter S, which takes into account the number of parameters used to describe the model defined by a given number of structure factors, was introduced into the program[62]:

$$S = \sqrt{\frac{\Sigma w|\Delta|^2}{N-NP}}$$

Atomic radii used in the program are those of Pauling[63]. Scattering factors for all non-hydrogen atoms are those of Cromer and Mann[64], and those for hydrogen atoms from Stewart *et al*[65].

As the original program commits the user to complex scattering factors from the start, and Hamilton's test on absolute structures is valid only for comparisons between non-dispersion-refined structures, a feature was introduced in the program whereby f'' could be set to 0.00 or to -f''.

PARST[66]: for calculation of orthogonal coordinates, bond distances (e.s.d.'s following Cruickshank[67]), torsion angles[68], weighted least-squares planes (e.s.d.'s after Stanford and Waser[69]), and intermolecular contacts. The program enables the comparison of coordinates of atomic subsets.

PLUTO[71]: for the plotting of individual molecules and packing diagrams. (Hydrogens were not included in these diagrams.)

EENY[72]: for various potential energy calculations. PE curves

were calculated for C, H, N and ME[73], while S and Ni atoms were considered ME-groups.

SHELXS-84[74]: a new direct methods program, was used in an attempt to achieve phasing in a pseudosymmetric structure.

C H A P T E R 3

CHAPTER 3

RESULTS AND DISCUSSION

3.1 The Host and Host-Guest Complexes of the Nickel Complex made with Racemic (*dl*)-α-Phenylethylamine

3.1.1. Initial characterization of the host complex and its clathrates

a) Microanalysis

The host complex $Ni(NCS)_2(dl\text{-}\alpha\text{-phenylethylamine})_4$ was analysed for percentage carbon, hydrogen and nitrogen content:

Found	61.9 %C	6.7 %H	12.7 %N
Calculated	61.3 %C	6.6 %H	12.7 %N

Similar results were obtained both from the washed, dried but unrecrystallized material aswell as a collection of crystals from a solution in methanol. (The latter are unstable in air and analysis of crystals which have been dabbed dry was carried out promptly after removal from solvent evaporation conditions.)

The unrecrystallized clathrate with *sec*-butylbenzene does not appear in the same dry state after washing and vacuum drying for a short period, and is unsuitable for microanalysis owing to loss of weight (solvent or guest compound evaporation). After the clathrate was vacuum dried for an extended period (48 hours), it had the following composition:

Found	56.9 %C	6.0 %H	12.3 %N

This corresponds more closely to the diamine complex

$Ni(NCS)_2(\alpha\text{-phenylethylamine})_2$:

Calculated	51.8 %C	5.3 %H	13.4 %N

The large discrepancy between observed and calculated values indicates possible incomplete decomposition and contamination. However, single crystals of the clathrate from a methanol solution produced the following results:

Found	66.1 %C	7.1 %H	10.3 %N

The theoretical values for the 1:1 complex between the tetramine complex and *sec*-butylbenzene are:

Calculated	66.6 %C	7.4 %H	10.6 %N

These correspond closely to the observed values for the clathrate crystals, which could thus be expected to correspond to a 1:1 host-guest complex.

Similarly, the analyses of the clathrate with *o*-xylene were reliable only when performed on crystals obtained from a methanol solution and dabbed dry before analysis:

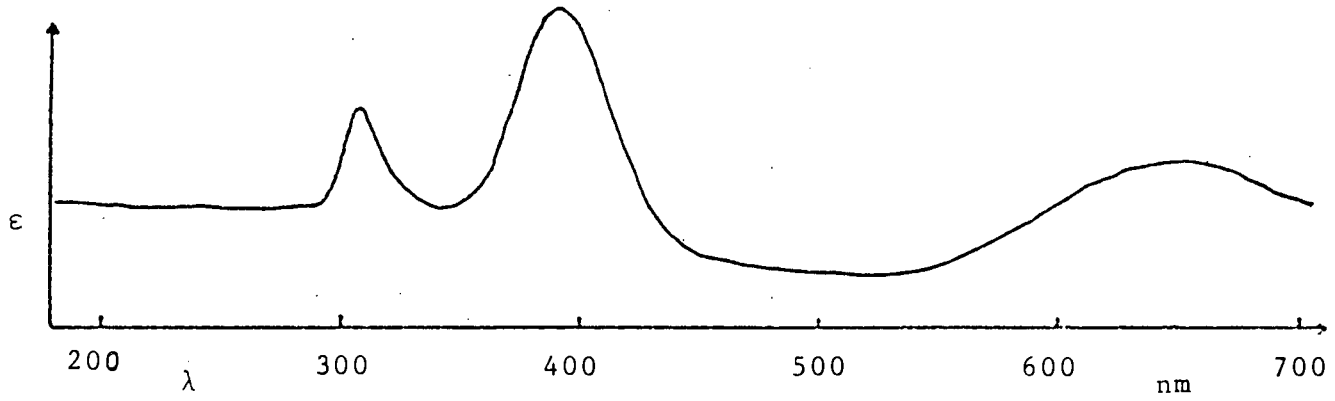
Found	66.6 %C	7.1 %H	10.2 %N

The experimental analysis here corresponds only roughly to that expected for a 1:1 complex:

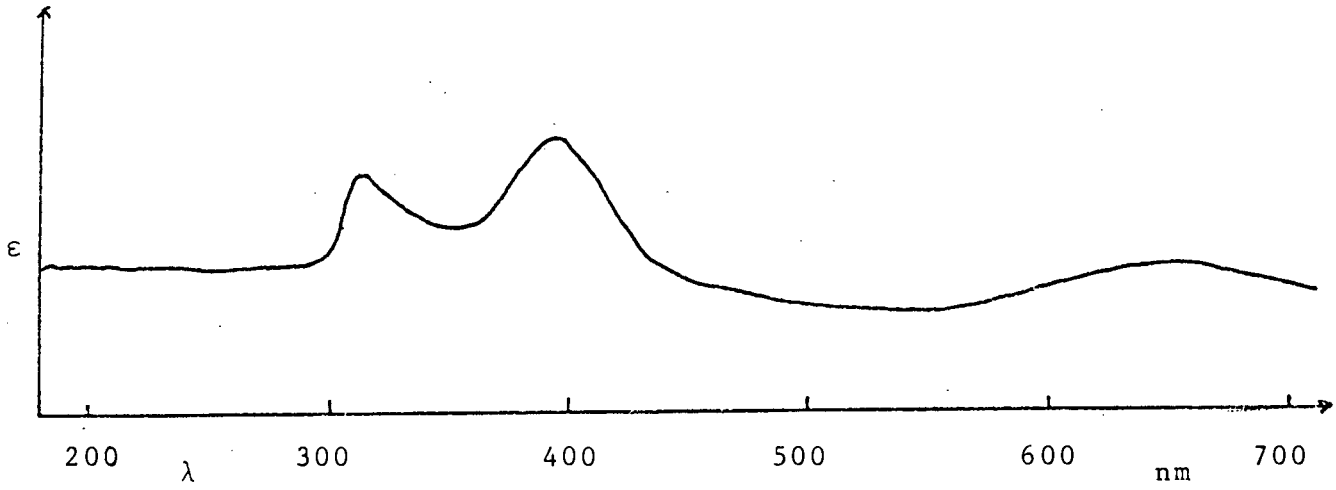
Calculated	70.1 %C	6.1 %H	9.5 %N

b) UV - Visible Spectroscopy

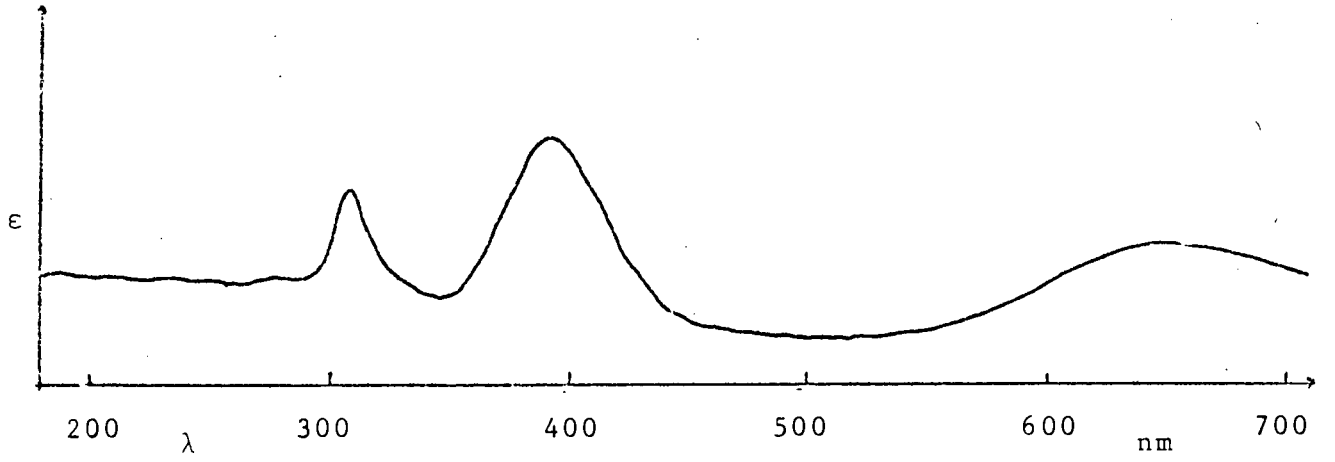
The spectra of the host complex and clathrates between 190 and 700nm are shown in Fig.3.1. The substances were dissolved



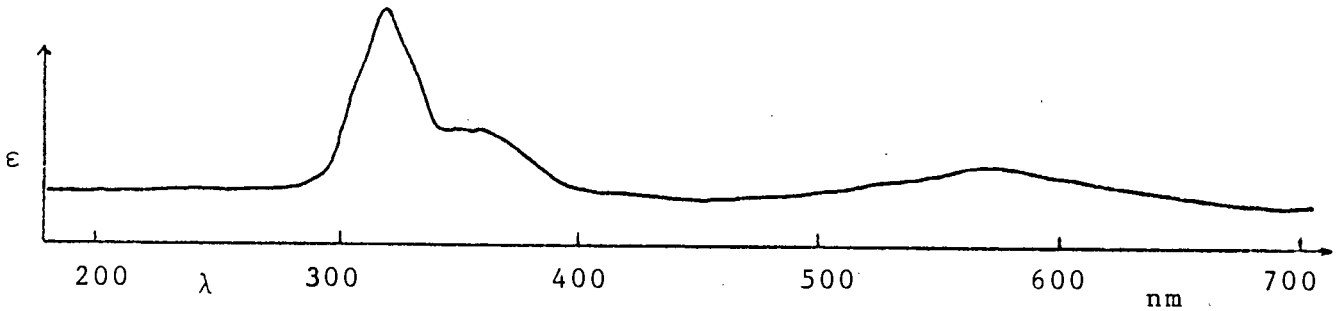
(a) Absorption spectrum of $[Ni(NCS)_2((dl)\text{-}\alpha\text{-phenylethylamine})_4]$



(b) Absorption spectrum of the *sec*-butylbenzene clathrate



(c) Absorption spectrum of the *o*-xylene clathrate



(d) Absorption spectrum of $[Ni(NCS)_2(4\text{-EtPy})_4]$ in CCl_4

Figure 3.1

in methanol. For comparison a spectrum of the $Ni(NCS)_2(4\text{-}EtPy)_4$ complex is shown in Fig. 3.1d.

A peak at ≃304nm appears in the absorption spectrum of the amine ligand, which is still observed in the spectra of the nickel complexes. This band does not appear to be a result of $n \rightarrow \pi^*$ transitions of the primary amine (expected at 190 - 200nm[76]), nor the $\pi \rightarrow \pi^*$ transitions of substituted benzene (expected at 230-250nm, 200-220nm and ≃180nm[77]), and may be the result of intermolecular $\pi \rightarrow \pi$ interactions.

Two other peaks attributable to ligand field effects of the nickel complexes appear at ≃396nm and ≃644nm, corresponding to the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transitions of octahedrally coordinated Ni^{2+} respectively. These peaks were assigned on the basis of their positions and relatively low intensities, the latter confirming that they are spin allowed but Laporte forbidden, as required by *d-d* transitions. The third principal absorption band, $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ from which a direct estimate of 10Dq can be obtained, lies beyond the instrumental range, but can be estimated at ≃950nm by the use of an Orgel diagram. (See Appendix 3 for the construction of an Orgel diagram for Ni(II) d^8 octahedral.) No additional, resolved peaks are observed in the spectra of the host-guest complexes. Electronic intermolecular host-guest interactions are therefore not indicated, remembering that such processes give rise to totally allowed transitions and therefore more intense absorptions.

The difference in colour between solutions of the typically blue substituted pyridine-type Werner clathrate and the greenish-blue α-phenylethylamine complex is evident from the

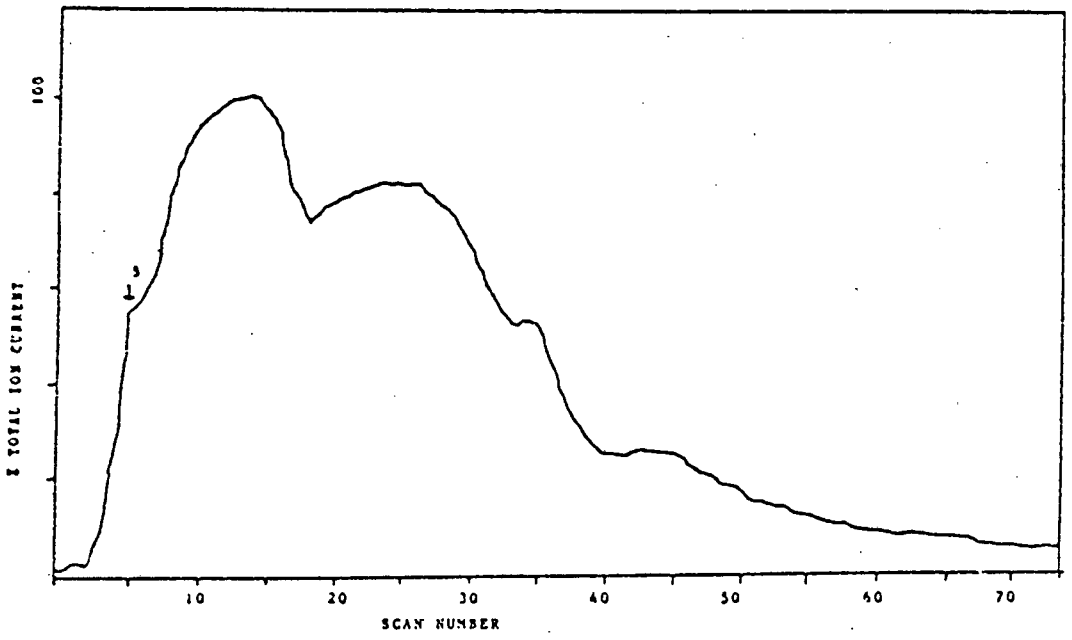
absorption peaks observed in the yellow and red regions aswell as the violet region of the visible spectrum. Compared to the 4-EtPy complex, the phenylethylamine complex has corresponding bands shifted to a higher wavelength, as can be seen in Fig.3.1. This may imply that the α-phenylethylamine complex has a lower value of 10Dq, and hence is less stable than the 4-EtPy complex.

c) Mass Spectroscopy

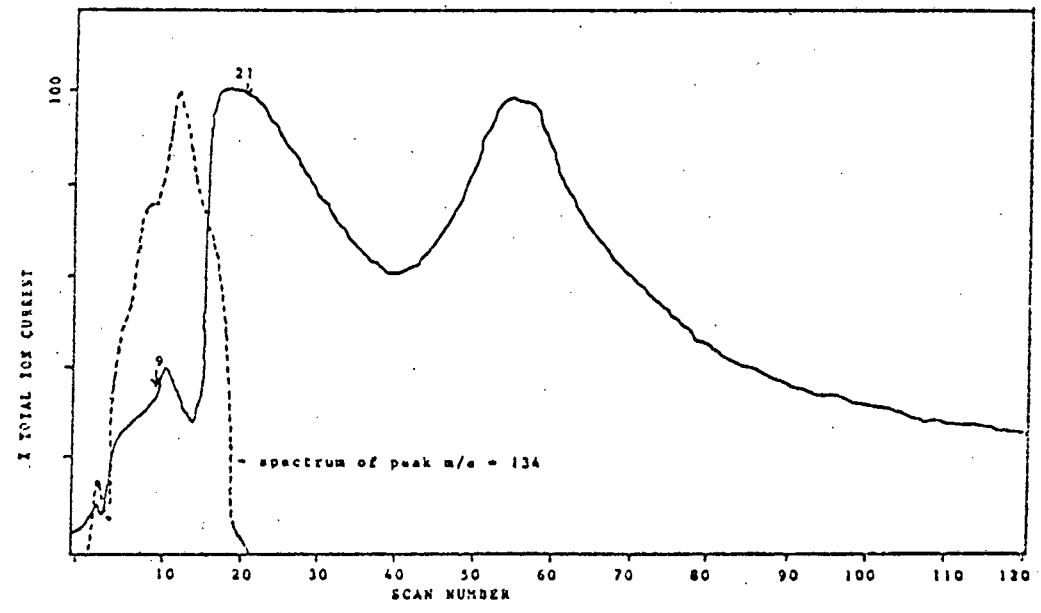
The total ion current spectra of the nickel host complex and its clathrates are shown in Figure 3.2, and the fragmentation patterns are outlined in Table 3.1.

The fragmentation patterns of the host complex were the same throughout. A weak molecular ligand radical peak (m/e = 121) was observed, but the most intense peak is m/e = 106.

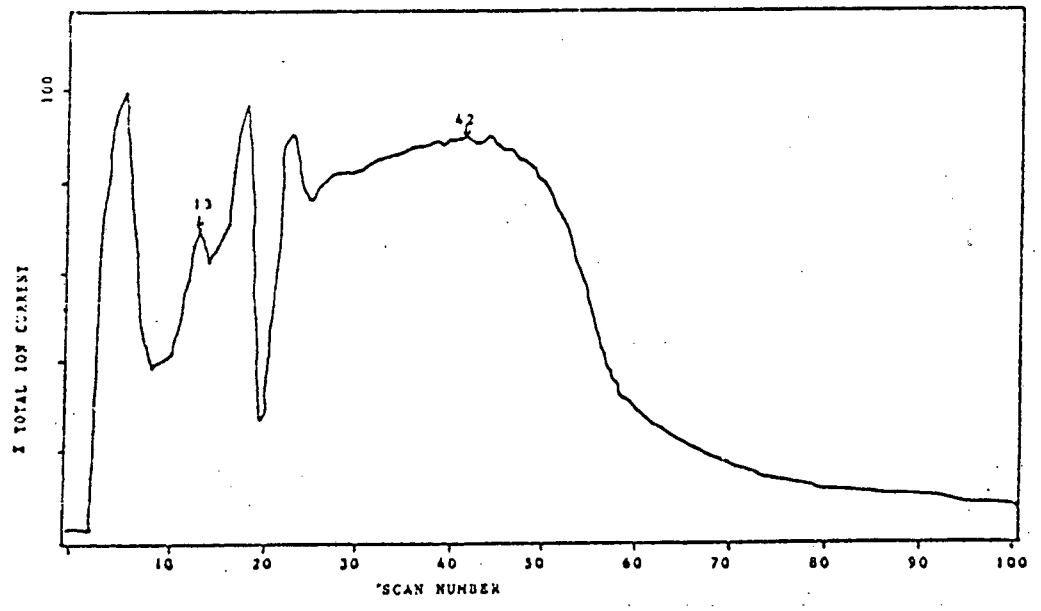
The total ion currents of the clathrates (unrecrystallized) have a somewhat more complex form than that of the host complex. However, as can be seen from the ion current for the m/e = 134 peak, the guest compound appears only in the first few scans, while all later scans are very similar to those of the pure host complex. In the fragmentation patterns of the early scans of the *sec*-butylbenzene clathrate, the important new peaks are of the molecular radical (m/e = 134), and m/e = 105 and 91. In the fragmentation patterns of the *o*-xylene clathrate, the only important, significantly altered peak is that at m/e = 91, as the molecular radical peak coincides with the m/e = 106 radical of the host ligand, as do the other important fragmentation peaks of the guest compound.



(a) Total ion current spectrum of the *dl*-ligand host complex



(b) Total ion current spectrum of the *sec*-butylbenzene clathrate



(c) Total ion current spectrum of the *o*-xylene clathrate

Figure 3.2

TABLE 3.1

(a) MASS SPECTRUM OF $Ni(NCS)_2$(*dl*-α-PHENYLETHYLAMINE)$_4$–

SCAN NO. 5

m/e	Relative % Abundance	Possible Inference
28	21	N_2^+
42	12	$C_2H_4N^+$
44	16	$C_2H_6N^+$
51	8	$C_4H_3^+$
53	9	$C_4H_5^+$
77	14	$C_6H_5^+$
79	24	$C_6H_7^+$
106	100	$C_7H_8N^+$
107	9	$C_7H_9N^+$
120	8	$C_8H_{10}N^+$
121	2	$C_8H_{11}N^{+\cdot}$

(b) ADDITIONAL PEAKS ARISING IN THE SPECTRUM OF THE *SEC*-BUTYLBENZENE CLATHRATE

SCAN NO. 9

Guest Compound

91	11	$C_7H_7^+$
105	78	$C_8H_9^+$
134	2	$C_{10}H_{14}^{+\cdot}$

(c) SIGNIFICANTLY ENHANCED PEAKS IN THE SPECTRUM OF THE *O*-XYLENE CLATHRATE

SCAN NO. 13

Guest compound

91	48	$C_7H_7^+$

d) Gas Chromatography

i) Column with racemic (*dl*)-ligand host

The retention volumes of the following organic compounds were determined at column temperatures of 54°, 60°, 64°, 70°, 75° and 82°C : *sec*-butylbenzene; *o*-, *m*-, *p*-xylene; chlorobenzene and *o*-dichlorobenzene. In all cases the carrier gas flow was 54.0 ml/min at 760mm and 60°C. The results appear in Table 3.2.

For closely related compounds the logarithms of the partition coefficients or relative retentions can be expected to be approximately a linear function of $1/T$[78]. A corresponding plot of logarithms of corrected retention volumes *vs* 1/T is shown in Fig.3.3.

The order of elution found for the above compounds is:

chlorobenzene < (*m*+*p*)-xylene < *o*-xylene < *sec*-butylbenzene < *o*-dichlorobenzene

Under the conditions described, a 1:1:1 mixture of xylenes could not be separated, but appeared as a single peak. As expected, no separation of the chiral *sec*-butylbenzene occurred by this column containing the racemic (*dl*)-ligand complex stationary phase. The relatively high retention of *o*-dichlorobenzene contradicts the assumption that, under comparable steric conditions, the greater the electron density in the aromatic ring of the 'guest' the greater the interaction with the aromatic ring of the α-phenylethylamine ligands.

It appears that the operating temperatures for these columns are severely limited: below ≈65°C the variation of relative

TABLE 3.2 UNCORRECTED RETENTION TIMES AND CORRECTED RETENTION VOLUMES FOR SOME AROMATIC COMPOUNDS ON A 30% (WT) $Ni(NCS)_2$(*dl*-α-PHENYLETHYLAMINE)$_4$ COLUMN

Column : length 100 cm

inner diameter 4 mm

Carrier gas : N_2

flow rate 54.0 ml/min

Compound	*54°C*	*60°C*	*64°C*	*70°C*	*75°C*	*82°C*
Petrol	23s	22s	21s	20s	20s	19s
	0.0ml	0.0ml	0.0ml	0.0ml	0.0ml	0.0ml
sec-Butylbenzene	232s	184s	150s	127s	108s	90s
	188.0ml	145.7ml	116.0ml	96.3ml	79.7ml	63.8ml
o-Xylene	85s	68s	57s	52s	49s	46s
	55.8ml	41.4ml	32.4ml	28.9ml	26.2ml	24.3ml
m-Xylene	72s	59s	53s	48s	45s	39s
	44.1ml	33.3ml	28.8ml	25.3ml	22.6ml	18.1ml
p-Xylene	73s	60s	52s	46s	43s	38s
	45.0ml	34.2ml	27.9ml	23.5ml	20.8ml	17.1ml
Chlorobenzene	62s	52s	48s	44s	42s	38s
	35.2ml	27.0ml	24.3ml	21.7ml	19.9ml	17.1ml
o-Dichlorobenzene	332s	268s	239s	197s	179s	145s
	278.0ml	237.4ml	176.1ml	159.3ml	143. ml	113.3ml

.retentions with inverse temperature ceases to be linear, and above 90°C the column begins to deteriorate. Between 65°C and 82°C the logarithm of the retention volumes is approximately a linear function of 1/T.

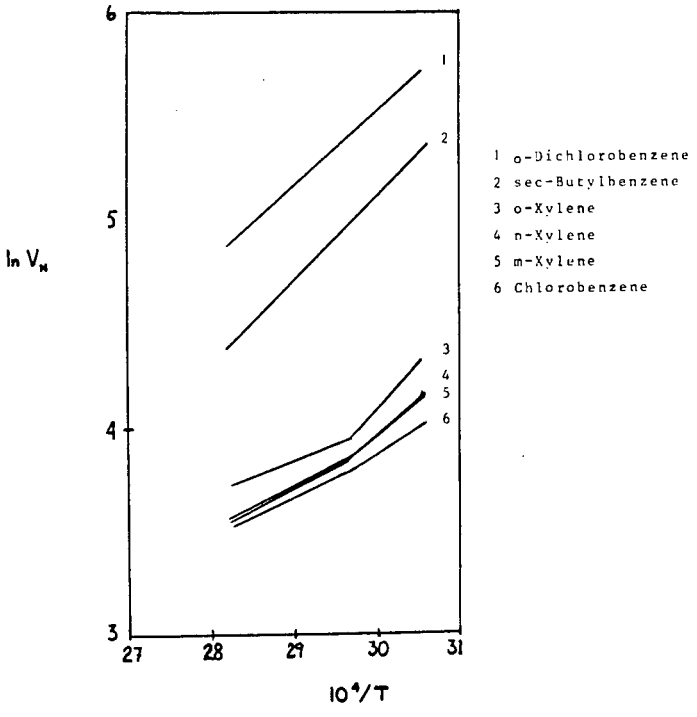


Figure 3.3 Temperature dependence of net retention volumes (V_n) for some aromatic compounds

ii) Column with (*dl*)-ligand complex clathrate with *sec*-butylbenzene

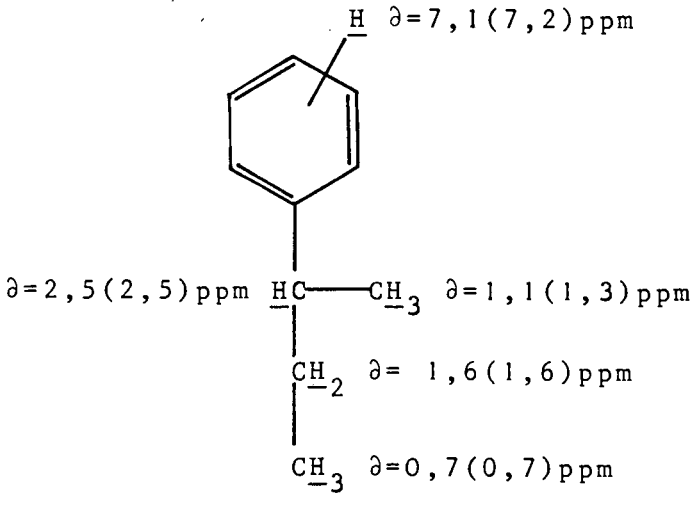
Chromosorb W was coated by dissolving it with the clathrate in methanol and subsequent rotary evaporation of the solvent. The column so prepared gave the same results as the column packed with only the host complex. However, it is suspected that the process of dissolving the clathrate and vacuum-evaporating the solvent thereafter destroys the clathrate structure, leaving a structure similar to the host complex used in the column described earlier. As the clathrate, in

its 'solid' state, dissociates already at ≈60°C, it appears unsuitable for direct application in gas choromatography.

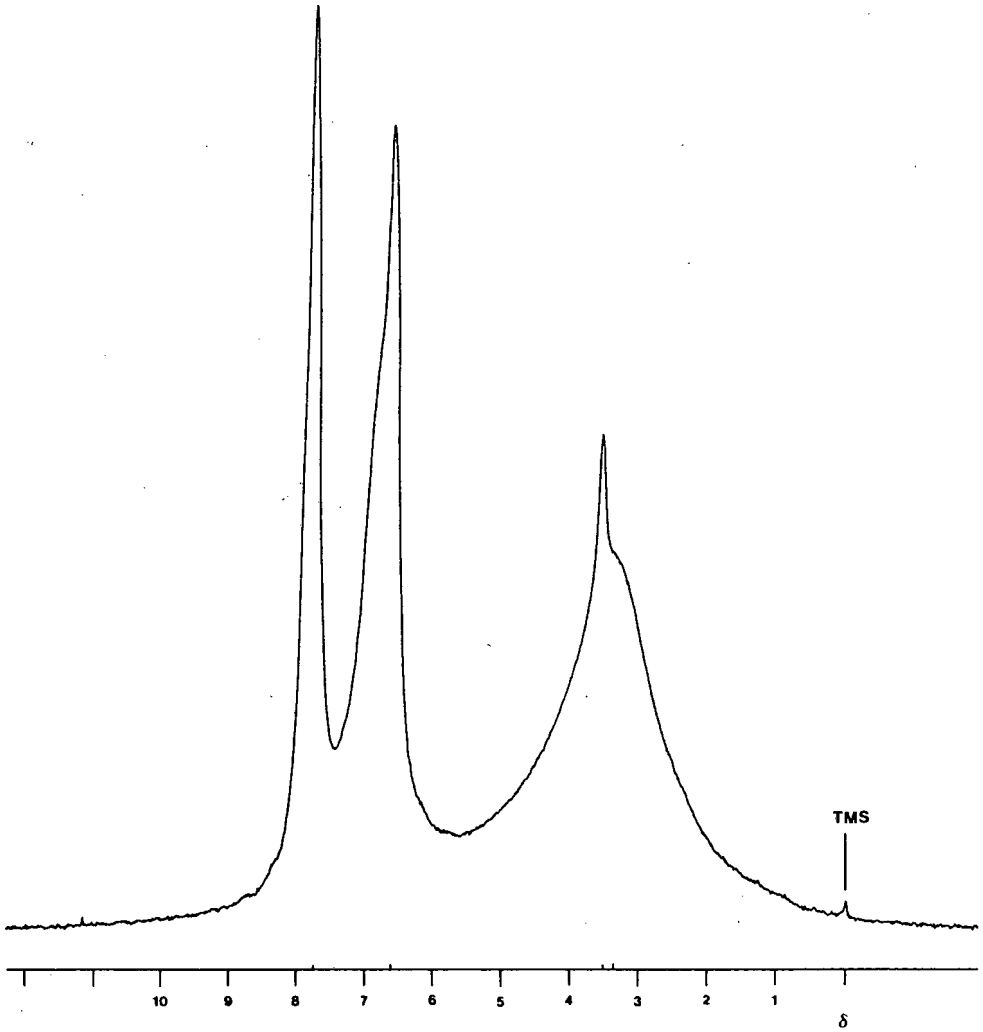
e) Nuclear Magnetic Resonance Spectroscopy

The NMR spectra of the host complex and *sec*-butylbenzene clathrate at room temperature (27°C) and -80°C, aswell as a spectrum of the dissolved host complex with *sec*-butylbenzene added to the solution are shown in Fig. 3.4.

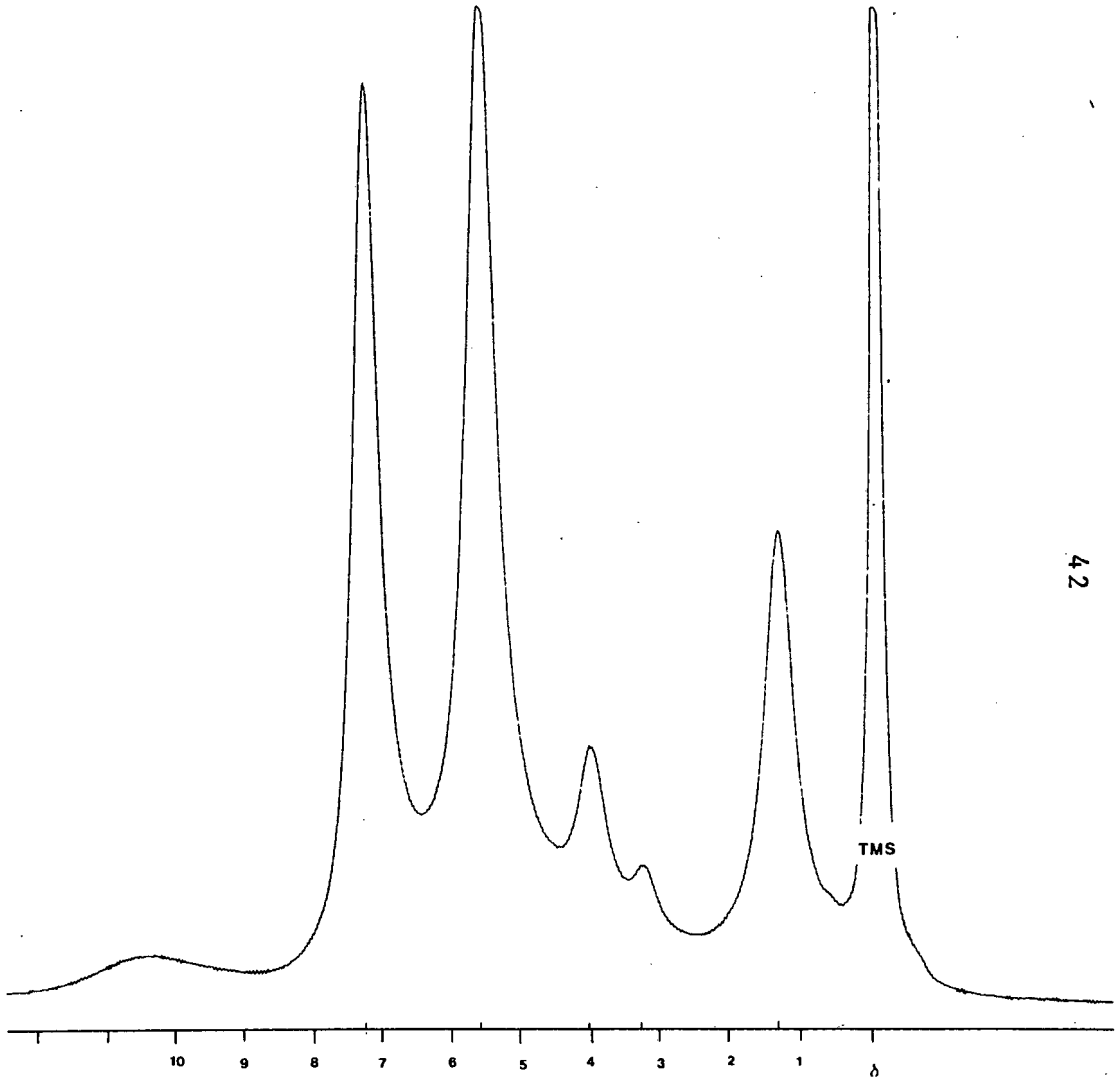
The small shifts caused by the paramagnetic Ni indicate that no conjugation between the Ni and the aromatic ligand exists, and the spectra are consequently limited to between δ=0-10ppm. In the R.T. spectrum of the host complex one broad and three sharp peaks appear. In the R.T. spectrum of the clathrate, five new peaks appear, which can be assigned to the guest compound as follows: (Shifts at -80°C in parentheses)



These resonance shifts are identical to observed shifts in the R.T. spectrum of the dissolved host with some added *sec*-butylbenzene. The remaining peaks, from the amine ligand, also show no significant differences in the two cases. If, in solution, there does exist a difference between the true clath-

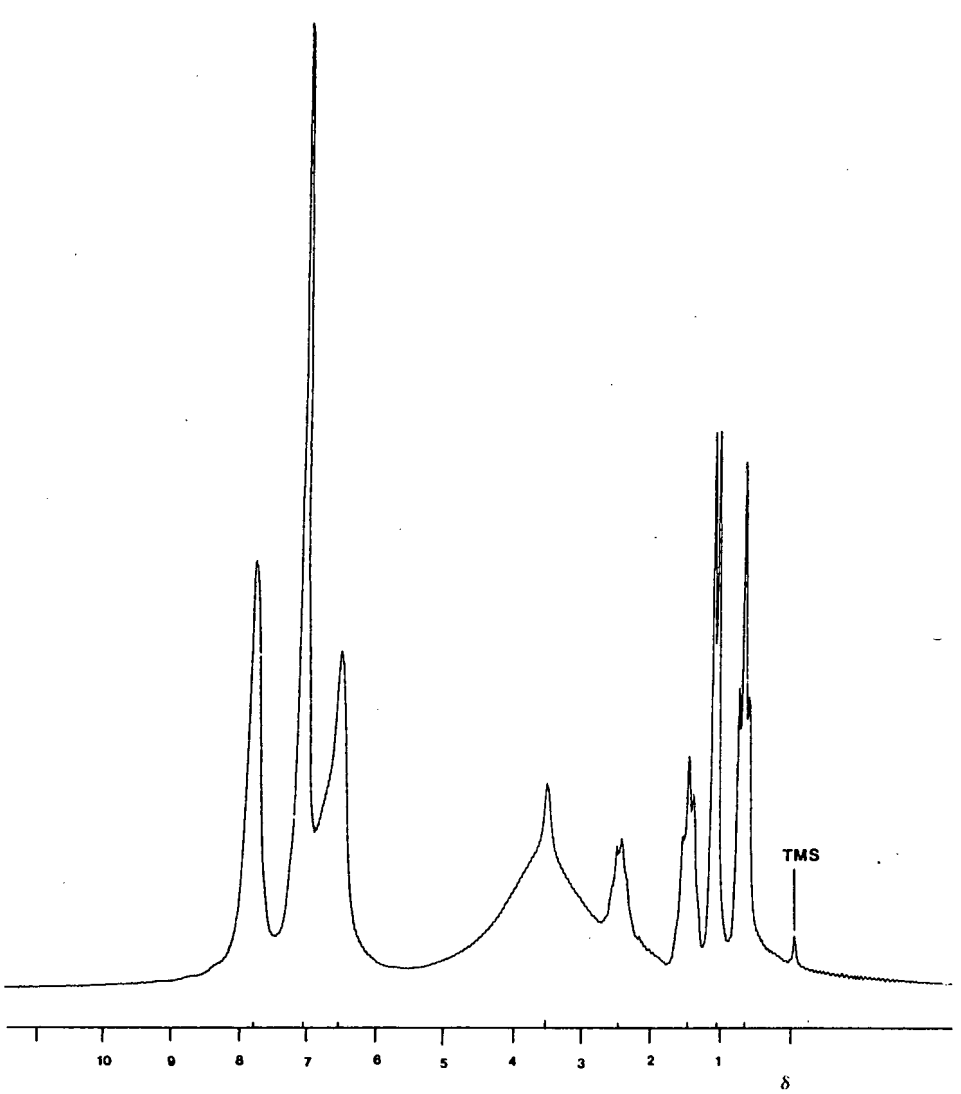


(a) The ^{1}H NMR spectrum of the host complex : 27^{o}C

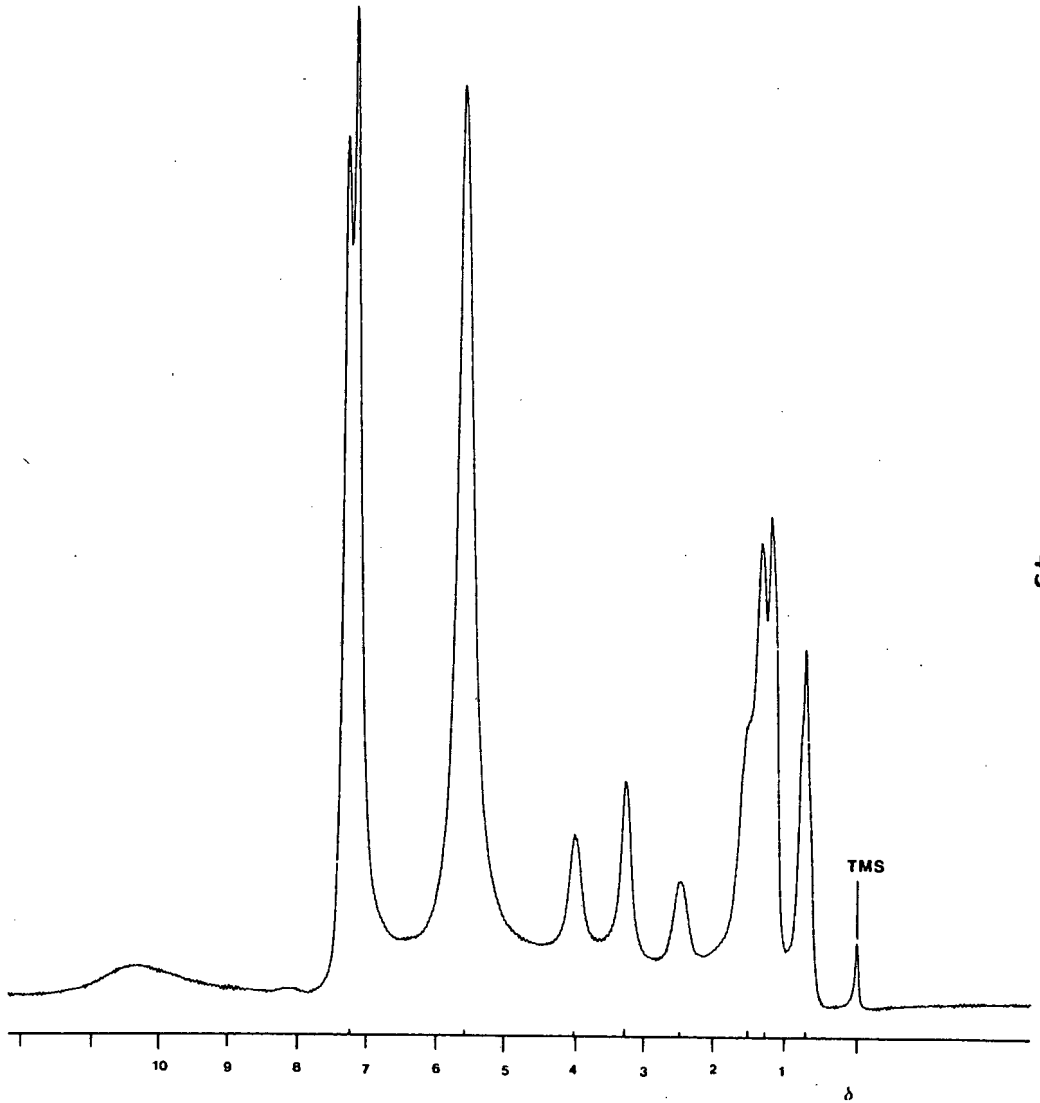


(b) The ^{1}H NMR spectrum of the host complex : -80^{o}C

Figure 3.4

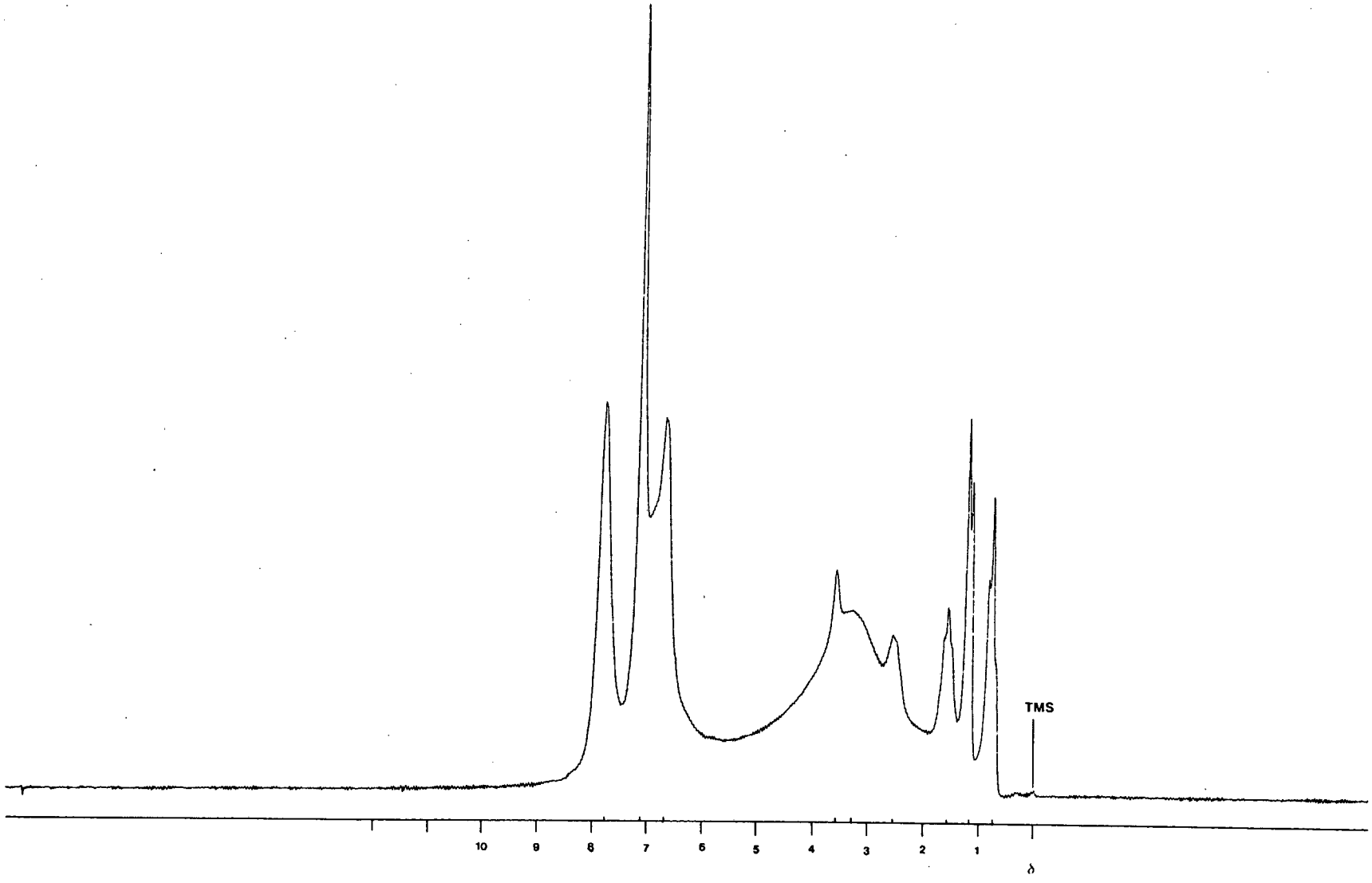


(c) The ^{1}H NMR spectrum of the sec-butylbenzene clathrate $27^{o}C$



(d) The ^{1}H NMR spectrum of the sec-butylbenzene clathrate $-80^{o}C$

Figure 3.4



(e) The ^{1}H NMR spectrum of the host complex dissolved in CD_3OD with an added quantity of sec-butylbenzene

Figure 3.4

rate and a solution mixture of the host complex and guest compound, these can thus not be told apart by ordinary NMR techniques.

The pure amine in CD_3OD has peaks at δ=1.3(-C$\underline{H}_3$), δ=3.9(*tert*-C$\underline{H}$), δ=4.3(-N$\underline{H}_2$) and δ=7.3(aromatic -C$\underline{H}$). The -N$\underline{H}_2$ peak is fully observed, indicating little or no proton exchange with the CD_3OD. Assignment of the ligand shifts in the nickel complex, however, is non-trivial, because of the shifts caused by the paramagnetic nickel.

Attempts to obtain assignments by extrapolation of a variable temperature study failed, because the relationship between chemical shift and inverse temperature is not linear over the experimental temperature range (see Fig. 3.5). A Curie law[79] is approximately obeyed at low temperatures (< -40°C), and while four peaks are observed at R.T., the host complex spectrum contains six resolved peaks below -40°C. A possible explanation for this is that, at relatively low concentration, conformational interchange processes occur which are rapid at room temperature, but that two distinct isomers are observed at low temperature.

The peaks in the R.T. host spectrum (Fig. 3.4a) at δ=6.6 and 7.7, integrating for the five aromatic hydrogens, coalesce at -40°C. They also decrease in intensity, and a new peak appears (δ=5.6 Fig. 3.4b). This latter peak may be assigned to the aromatic hydrogens of the second isomer. The low broad peak at δ=10.3 (-80°C) appears to result from the -N$\underline{H}_2$ hydrogens, as the shift change of these can be expected to be greatest. The sharp peak at δ=3.5 hardly shifts at all, and is attributable to the *tert*-C$\underline{H}$. A broader peak shifts from δ=3.3 to

δ=1.3 between R.T. and -80°C and is hence from -C$\underline{H}_3$ hydrogens. A small peak appearing at δ=4.1ppm (Fig. 3.4b) may be owing to -C$\underline{H}_3$ hydrogens of the same isomer giving rise to the aromatic -C$\underline{H}$ shift at δ=5.6 in the same spectrum.

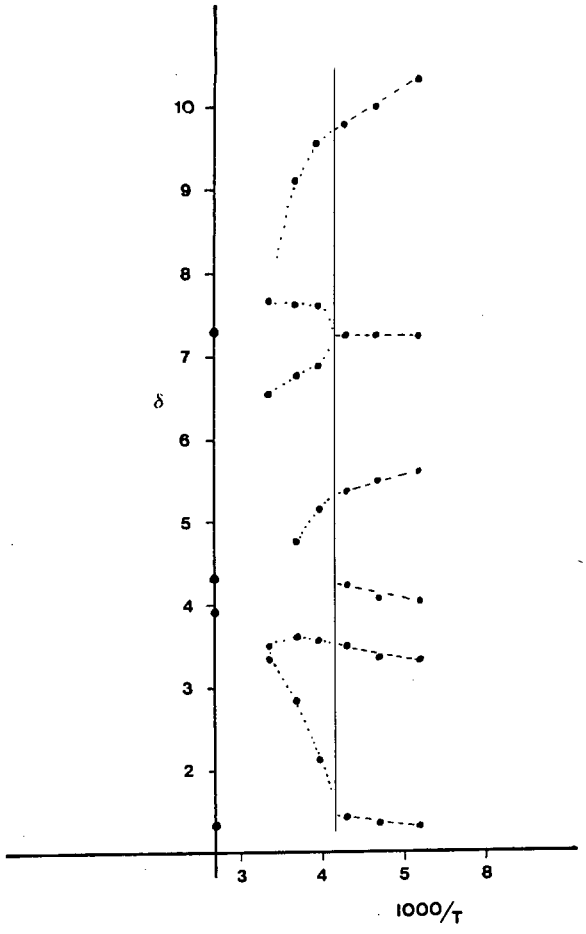


Figure 3.5 Chemical shift (ppm) *vs* inverse temperature for the $Ni(NCS)_2(\alpha\text{-phenylethylamine})_4$ complex

f) INFRARED SPECTROSCOPY

The representations of IR spectra of the (*dl*)-ligand host complex and its *sec*-butylbenzene and *o*-xylene clathrates as Nujol mulls are shown in Fig. 3.6. The spectra of the clathrates after storage for 24hours as Nujol mulls are also shown.

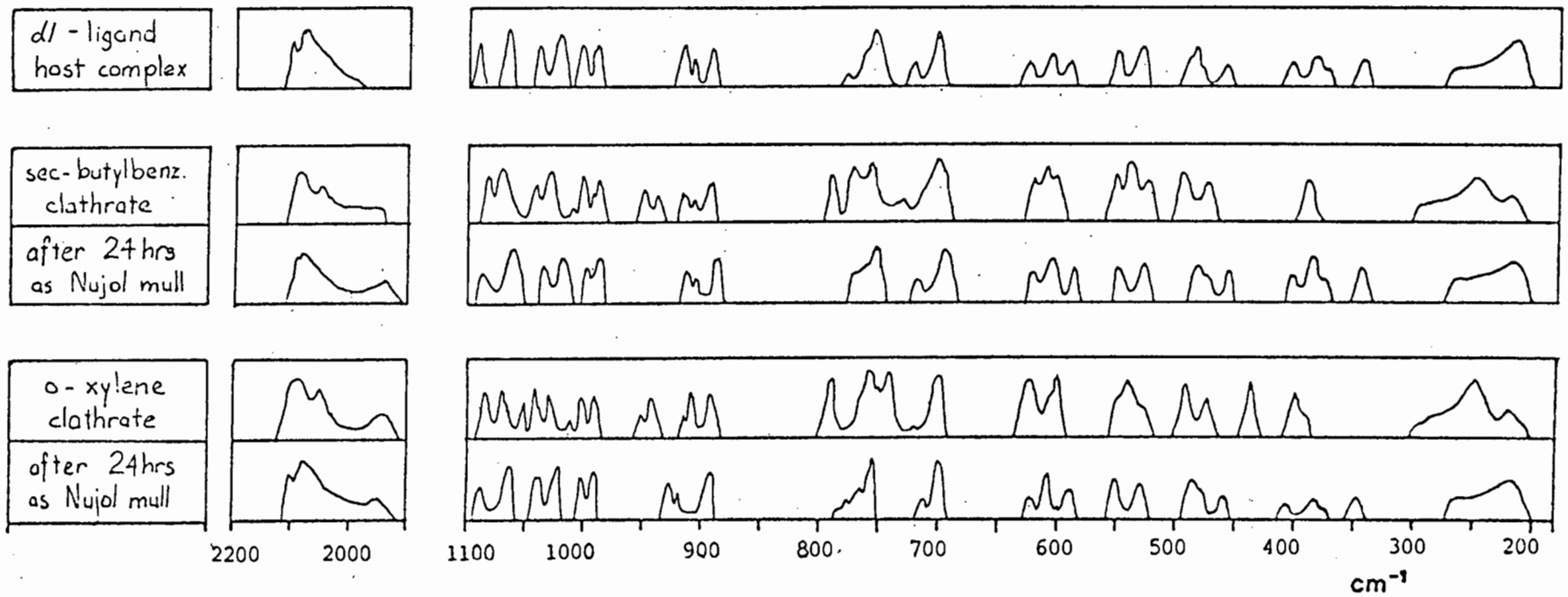


Figure 3.6 Represenations of the IR spectra of the *dl*-ligand host complex and its *sec*-butylbenzene and *o*-xylene clathrates as Nujol mulls

The spectra cover the range μ = 2200 - 1900cm^{-1} and μ = 1100 - 190cm^{-1}.

Peaks were assigned by comparison with the IR spectra of $[Ni(NCS)_2(py)_4]$ and $[Ni(NCS)_2(py)_2]$[80], $[Ni(an)_2Cl_2]$ and $[Ni(an)_2Br_2]$[81], $[Ni(NCS)_2(an)_2]$ and $[Ni(p\text{-toluidine})_2(NCS)_2]$[56]. Observed peaks and possible assignments are listed in Table 3.3.

The most remarkable observation from the spectra is that, after storage as a Nujol mull, the clathrates give rise to spectra resembling that of the host complex. Given the x-ray crystal structure information this implies that, as a Nujol mull at room temperature, the *trans*-complex of the clathrate structure reverts to the *cis*-complex as observed in the host structure.

This also explains the previously reported absence of the clathrate band at about 800cm^{-1} after storage[54]. The υ_{N-CS} bands in the clathrates appear at ≈2093cm^{-1} with shoulders at ≈2051cm^{-1}, while a shoulder is observed on the high-wave-number side of the strong peak after storage. The host structure does not give rise to two resolved bands of similar intensity assignable to υ_{N-CS} as expected, and only one strong band is observed.

In the host and stored-clathrate spectra four bands (three resolved at 348, 389 and 408cm^{-1}, a shoulder at ≈365cm^{-1}) are observed which correspond to υ_{M-NH_2} for the amine ligand nitrogen-metal vibrations. The clathrate spectra show only one band at ≈400cm^{-1}, having a shoulder at ≈385cm^{-1} (*o*-xylene clathrate) and 410cm^{-1} (*sec*-butylbenzene clathrate). The number of bands expected from symmetry calculations is thus observed

TABLE 3.3 ABSORPTION PEAKS AND SOME POSSIBLE ASSIGNMENTS (VALUES IN cm^{-1})

dl-ligand host	*sec*-butyl-benzene clathrate	clathrate after 24 hours as Nujol mull	*o*-xylene clathrate	clathrate after 24 hours as Nujol mull	Assign-ment
2089	2093	2091	2096	2088	νN-CS
1090	1082	1090	1085	1090	
1065	1070	1065	1071	1064	
1039	1037	1039	1041	1039	
1022	1027	1022	1025	1022	
1003	1002	1002	1002	1003	
992	988	992	989	992	
917	936	916	945	917	
909	908	909	911	909	
893	895	893	895	893	
851	849	850	841	851	
757	757	757	760	757	νNC-S
722	730	722	742	722	
699	703	700	698	699	
625	620	625	624	623	NH_2 wag
608	609	607	606	608	
589	600	590	601	589	
553	552	553	551	553	
532	541	531	542	553	NH_2 rock
	524		526	532	
486	497	487	494	486	
479	475	480	475	478	δNCS
459		459	437	459	
408		407		408	
388	400	386	400	388	νNi-N
365	393	368	387	368	νNi-N
349		347		349	
	256		249		
222	218	222	219	222	νNi-NCS

(refer to 2.3.6 and Appendix 2).

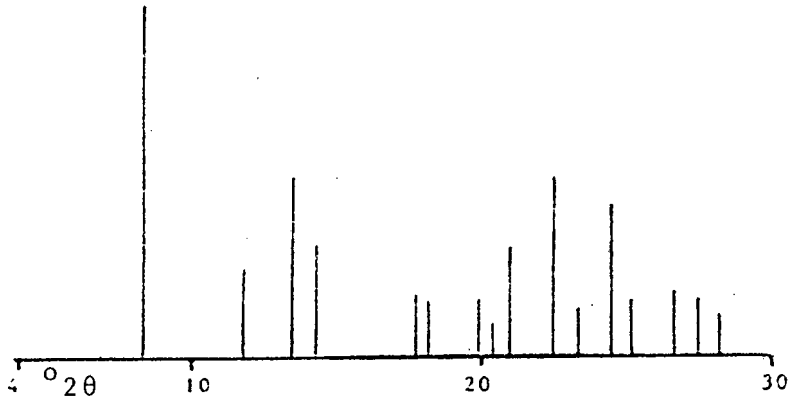
A strong υ_{M-NCS} band appears in the host and stored-clathrate spectra at 222cm^{-1} with a shoulder at higher wavenumber, while two bands at ≈220 and 250cm^{-1} (strong) are observed in the clathrate structures. (Any further bands at lower wavenumbers are obscured by absorption of the CsI cells.) In this case the expected number of bands does not agree with that observed, if both of the clathrate bands are indeed due to υ_{M-NCS}.

Owing to the structural differences of the nickel complex as host structure and in the clathrates, the inspection of IR spectra affords a ready answer as to whether a clathrate has been formed or not. Band assignments are only by comparison and somewhat tentative, agreement with theoretical predictions not being absolute.

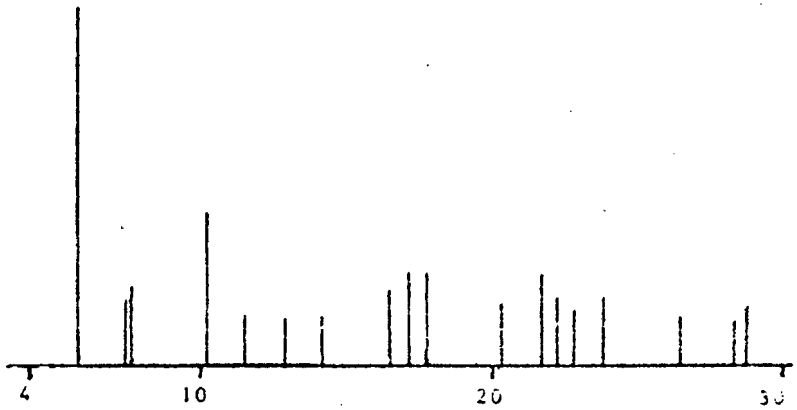
g) X-Ray Powder Diffractometry

The x-ray diffractograms of the (*dl*)-ligand complex and its *sec*-butylbenzene and *o*-xylene clathrates are shown in Fig.3.7.

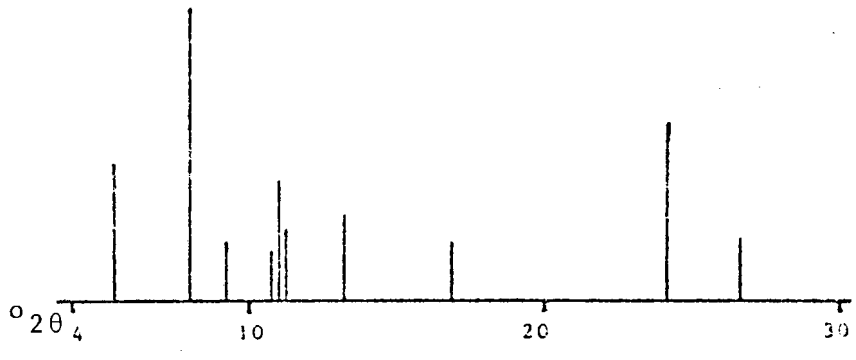
The spectra of the host complex and both clathrates are all different from each other, which indicates that different crystalline forms arise for each species. Vacuum drying of the *sec*-butylbenzene clathrate for 2 hours at 40°C resulted in a collapse of the crystalline form, and only one broad peak between 2θ = 6 and 7° was observed. However, after about 48 hours of vacuum drying at 40°C the diffractogram represented in Fig. 3.7d was obtained. The spectrum does not resemble that of the host complex, and microanalytical results suggest that a diamine complex was formed (see 3.1.1a).



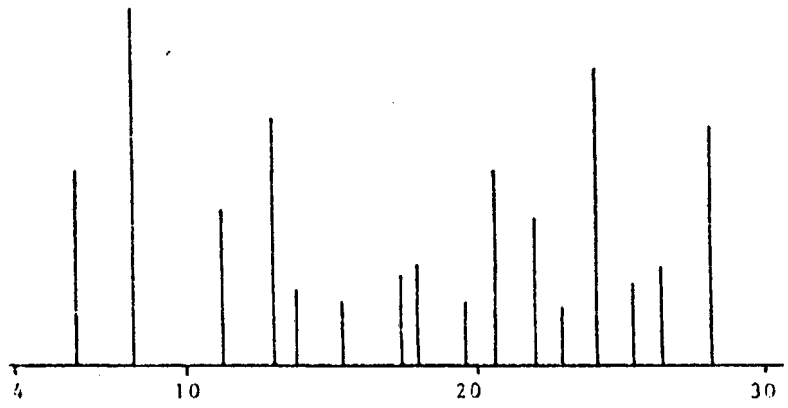
(a) Host complex



(b) Clathrate with *sec*-butylbenzene



(c) Clathrate with *o*-xylene



(d) *Sec*-butylbenzene clathrate after 48hrs of vacuum drying

Figure 3.7 X-Ray Powder Diffractograms

x-ray powder diffractometry therefore is a further suitable technique to determine whether a clathrate with this particular host complex has been formed, and to determine whether the clathrate structure has degraded after storage.

3.1.2 Single Crystal Structures

a) The Crystal and Molecular Structure of 1:1 $[Ni(NCS)_2((R)$-α-phenylethylamine$)_4]$: $[Ni(NCS)_2((R)$-α-phenylethylamine$)_2((S)$-α-phenylethylamine$)_2]$

i) Preliminary X-Ray Analysis and the Determination of the Space Group

An oscillation photograph of a single crystal of the Ni-complex which was made from racemic α-phenylethylamine, showed m_x symmetry when the crystal was rotated about its long axis. This indicated a monoclinic or higher space-group[82]. The axis measured ≃14.3Å.

Weissenberg photographs (zero-layer photograph depicted in Fig. 3.8) seemed to indicate a tetragonal space-group. Two axial lines are separated by 90°, and the reflections on both appear to be spaced by equal distances, resulting from two axes of the same length. From these photographs two cell choices were apparent depending on whether one considered the more intense straight lines of reflections to be the reciprocal layer lines, or instead those exactly 45° between them, which are less intense. The ways in which the reflections could be indexed are displayed in Fig. 3.9.

The two unit cells derived are:

a ≃ 22.0Å	c ≃ 14.3Å	Z = 8¶
a ≃ 15.6Å	c ≃ 14.3Å	Z = 4

¶*Calculated by dividing cell volume by a molecular volume based on a 19Å^3 average volume for each non-hydrogen atom.*

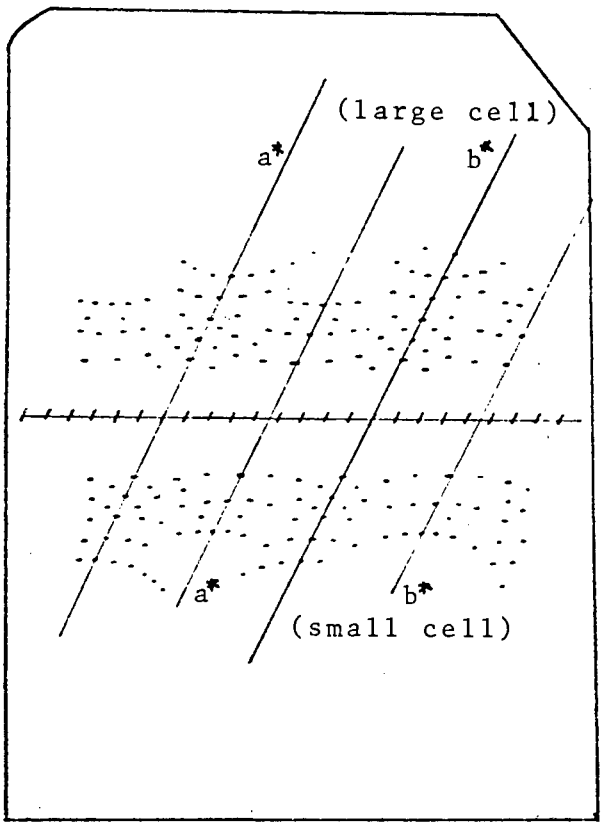


Figure 3.8 Zero-layer Weissenberg photograph about the long needle-axis

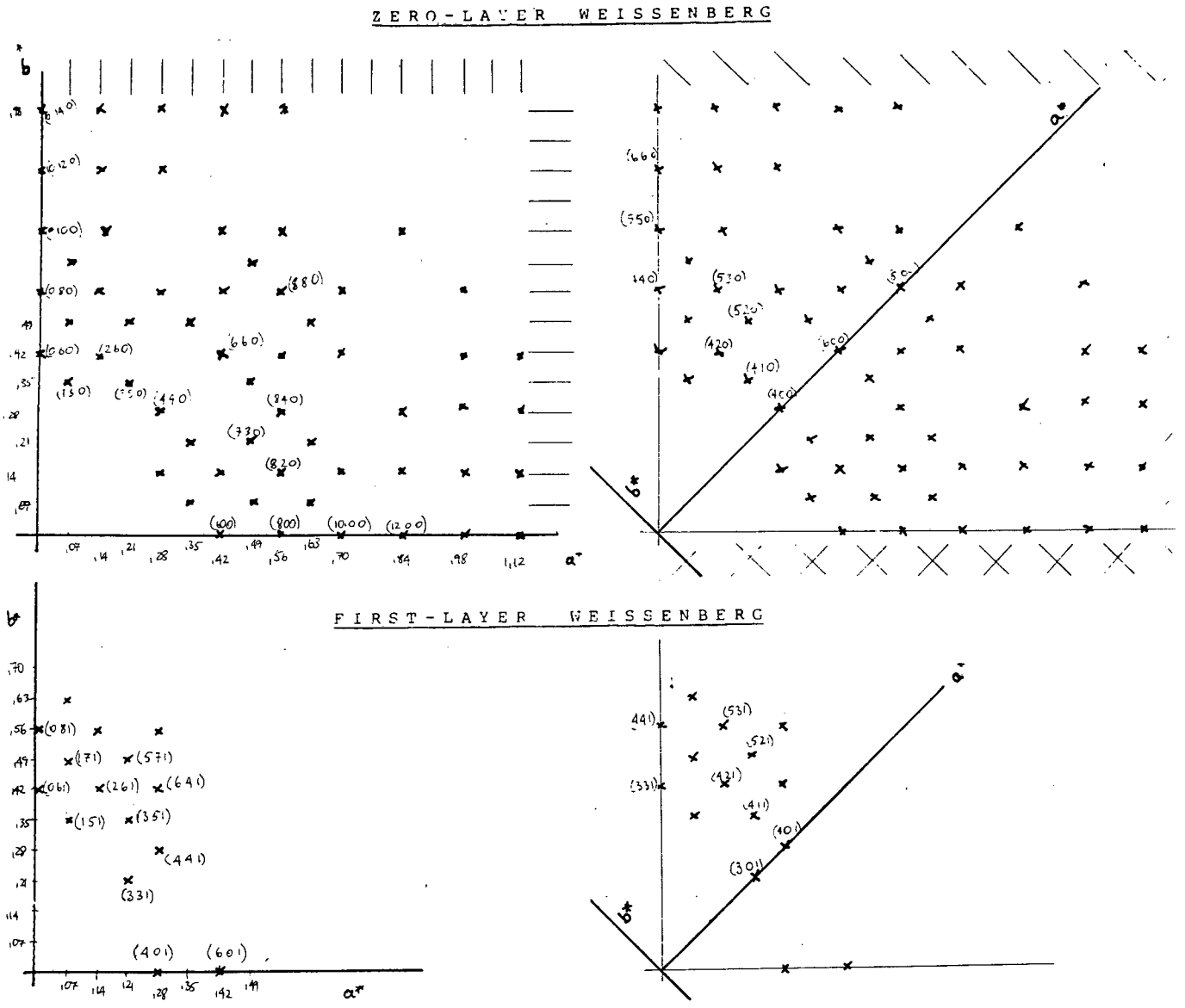
Since there is no tetragonal space-group accommodating the reflection conditions applying to the large cell, it was deduced that the correct cell choice was that of the small cell. Here the only condition for non-extinction was *(h00) : h = 2n.*

The preliminary X-ray analysis was thus indicative of the space-group $P42_12$ (No.90)[83].

Accurate cell dimensions measured on a diffractometer, however, yielded a non-tetragonal cell. Refined on 25 high-intensity reflections in the θ-range 10° - 17°, the cell parameters are:

a = 15.543(2)Å	b = 15.300(4)Å	c = 14.747(30)Å
α = 90.02(10)°	β = 89.90(10)°	γ = 89.82(2)°

An orthorhombic space-group was confirmed by testing the



a = 22.0Å

a = 15.6Å

Conditions for non-extinction

(h00): $h = 2n$

(hh0): $h = 2n$

(hk0): $h+k = 2n$

(hkl): $h+k = 2n$

(h00): $h = 2n$

Indexing reflections of the zero- and first-layer Weissenberg photographs in the large and the small unit cell.

Figure 3.9

relative intensities of Laue-symmetry related reflections. The results for one set of reflections are shown in Fig.3.10.¶

Minimum reflection requirements

Tetragonal	Orthorhombic
$\|F(hkl)\| = \|F(khl)\| =$	$\|F(hkl)\| = \|F(\bar{h}\bar{k}l)\|$
$\|F(\bar{h}\bar{k}l)\| = \|F(\bar{k}\bar{h}l)\|$	

Observed intensities

h	k	l	≃I	h	k	l	≃I
8	6	4	20	8	6	4	20
6	8	4	30				
-8	-6	4	20	-8	-6	4	20
-6	-8	4	30				
-8	-6	-4	20	-8	-6	-4	20
-6	-8	-4	30				
-8	6	4	20	-8	6	4	20
6	-8	4	30				
-8	6	-4	20	-8	6	-4	20
6	-8	-4	30				

Figure 3.10 Intensities of symmetry-related reflections in tetragonal and orthorhombic space-groups.

To ensure that no weak reflections which would have broken the condition *(hkl): h+k=2n* for the large cell had been unidentifiable on film, a trial data set was collected for the large cell. For l = 0 - 2, no *h+k=2n+1* reflection was observed, and

¶*In the light of the findings of the diffractometer, the photographs were reexamined. Acknowledging their poor quality, the small difference in cell dimensions* a *and* b *and the similarity of most I(hkl) to I(khl) had led to the initial erroneous crystal system assignment.*

the small orthorhombic cell was confidently reverted to as the correct cell choice. From the measured intensity data the following conditions of non-extinction were determined:¶

$$(h00): \quad h = 2n$$
$$(0k0): \quad k = 2n$$

The orthorhombic space-group corresponding to these reflection conditions is $P2_12_12$ (No.18), in which the structure was solved and refined.

ii) Intensity Data Collection

Accurate cell parameters were determined by least-squares analysis based on 25 high-intensity reflections in the θ-range $10^o < \theta < 17^o$. Higher θ reflections were regrettably too weak for this procedure on the CAD4. The orthorhombic space-group $P2_12_12$ is acentric and thus has[84]:

$$|F(hkl)| = |F(h\bar{k}\bar{l})| = |F(\bar{h}k\bar{l})| = |F(\bar{h}\bar{k}l)|$$
$$\neq |F(\bar{h}\bar{k}\bar{l})| = |F(\bar{h}kl)| = |F(h\bar{k}l)| = |F(hk\bar{l})|$$

No Bijvoet pairs were collected (refer to Appendix 1). The intensities of three standard reflections which were monitored periodically were stable to within 2.4% of their mean values. The diffractometer data set contained 3231 measured unique reflections of which 2233 satisfied the criterion $I_{rel} > 2\sigma I_{rel}$, which were used in the structure solution and refinement. All relevant crystal data are listed in Table 3.4.

¶*Note that these, in the orthorhombic space-group, are the same conditions as (h00): h=2n for the tetragonal space-group considered before.*

TABLE 3.4 CRYSTAL DATA

Molecular Formula	$C_{34}H_{44}N_6NiS_2$
Molecular Weight	$659.59 gmol^{-1}$
Space-Group	$P2_12_12$ (No.18)
a	15.543(2)Å
b	15.300(4)Å
c	14.747(29)Å
α	90.0°
β	90.0°
γ	90.0°
Volume	$3507(7)Å^3$
Z	4
D_c	$1.25 gcm^{-3}$
$\mu(MoK_\alpha)$	$6.53 mm^{-1}$
F(000)	1400
Crystal Dimensions	0.22 x 0.38 x 0.13mm
Scan mode	$\omega-2\theta$
Scan width	$(0.93+0.35\tan\theta)^\circ$
Vertical aperture length	4mm
Aperture width	$(1.32+1.05\tan\theta)$mm
Final acceptance limit	20σ at $20^\circ min^{-1}$ in ω
Maximum recording time	40 s
Crystal stability	2.4%
Range scanned	$1 - 20^\circ\theta$
Total number of reflections	3231
Final Refinement Data	
R	0.062
R_w	0.056
S	4.585
N	2233
NP	230

iii) Solution and Refinement of the Structure

The structure was solved by the heavy-atom method: the highest Patterson peaks, corresponding to NixNi vectors were:

x/a	*y/b*	*z/c*	*rel.intensity*
.0000	.0000	.0000	1.00
.0000	.0000	.5000	.34
.5000	.5000	.8344	.34
.5000	.5000	.1656	.34
.5000	.5000	.3301	.34
.5000	.5000	.6699	.34

This corresponds to the four Ni-atoms falling on the special positions

0, 0, z and .5, .5, $\bar{z}$ (Wykhoff letter *a*)

with z = 0.0828 and 0.0828 + .50. Interestingly, the space-group does not prescribe a (0,0,z), (0,0,z+.5) equivalence. The point symmetry of the Wykhoff position *a* is a two-fold axis, such that three ligands around each nickel atom need to be found.

When a difference Fourier map was calculated by inserting only the nickel atoms (R=0.43), six octahedrally orientated peaks at reasonable Ni-N distances (2.05 - 2.23Å) appeared around each Ni atom, *viz.*

	x/a	*y/b*	*z/c*
Ni	.5000	.5000	.0828
1	.6283	.4584	.1080
2	.6286	.5426	.1063
3	.5528	.4236	.1999
4	.5530	.5766	.1982
5	.5599	.4244	-.0134
6	.5597	.5759	-.0142

The symmetrical positions of these peaks indicate a pseudo-symmetry element, *viz.* a mirror in the *xz* plane.

It was hoped that arbitrary insertion of one of the mirrored -NCS groups which were apparent in the Fourier map would overcome the phasing problem. Instead, the resulting Fourier after least-squares refinement had no recognizable geometry and a higher residual than before (R=0.48). Mathematically, the phasing problem arises because in the calculation of the structure factors,

$$F_c = \sum_j f_j e^{2\pi(hx + ky + lz)}$$

the nickel atoms provide little information, as the term $(hx + ky + lz)$ is rendered near-zero for (x,y,z) = (0.0, 0.0, 0.083). In addition, the observed intensities in the almost-tetragonal cell are related by pseudo-symmetry, which is thus retained in the resulting difference map. Only after many trials a suitably descriptive model was found which allowed the structure to be solved. It is noteworthy that even when complete phenyl rings with acceptable interatomic distances were located by one L.S. Fourier calculation, insertion of the atoms in the next cycle of computations often shifted the atoms into a totally unrecognizable geometry.

The conventional residual R remained above 0.2, even when more than 75% of the scattering matter had been correctly located and the Ni and S atoms treated anisotropically. Eventually the residual dropped to below R = 0.1, and with all hydrogen atoms (except $-N\underline{H}_2-$) in calculated positions, Ni and S refined anisotropically, the residual obtained was R = 0.067. This structure, which was refined to $|\text{shift/esd}| < 1/50$, was subsequently inverted. The resulting residual, when all parameters in the opposite configuration had refined to the same degree as before, was R = 0.072.

$P2_12_12$ is a non-centro-symmetric space-group, for which an absolute structure should be determined. It may be argued, however, that little significance can be attached to the difference in the two residuals obtained above, because no Bijvoet pairs were measured. Moreover, Hamilton's test is not applicable to dispersion refined structures. The following, however, may be considered:

1) The nickel atoms are the strongest scatterers and also have the greatest anomalous scattering vectors. At low θ their contribution to the total scattering factor is small (location near origin on a special position), so that the lighter atoms instead become the major contributors to the scattering factors, allowing their relatively small anomalous scattering vectors to become more significant.

2) At high θ, when the Ni-contribution to the scattering factors becomes larger, its own anomalous scattering has become more significant because only the real part of the scattering vector decreases with increasing θ.

3) Inspection of the two dispersion refined structures reveals that inversion of the structure did not result in a shift of any parameter, such that the shift was greater than the e.s.d. of the parameter (except for one anisotropic temperature factor).

The modelled structure therefore appears to be firmly described by the measured intensities, with no systematic errors as a result of the omission of Bijvoet pairs. Consequently the dispersion refined structure with the lower residual was taken as correctly representing the absolute structure of the crystal.

In order to obtain an indication of the significance of the

difference between the correct structure and its inverse the program SHELX was adapted to allow the complex part of the scattering factor of all atoms to be set to zero. The hypothesis that the 'wrong' structure from above is in fact the better model could then be tested using Hamilton's test:

The structure obtained above was refined with f''= 0.0 for all atoms, giving rise to a coordinate set $+x_j$. Two sets of structure factors, F_c, were then calculated without any further refinement: one for the coordinate set $+x_j$, and one for the antipodal structure, $-x_j$. Both sets used the same isotropic thermal parameters and scale factor and $+if''$ for each dispersive atom. Two different residuals were obtained:

$$R^- = 0.0717 \qquad R^+ = 0.0677$$

Using Hamilton's test[85], the hypothesis that the structure which had earlier given the higher residual was a better model of the measured intensities, could be rejected at a significance level of 0.005 (see Table 3.5).

When the structure with the lower residual, $+x_j$, was refined with nickel and sulphur atoms treated anisotropically and all hydrogens of parent carbon atoms in calculated positions, peaks became apparent in the electron density maps corresponding to hydrogens of the amine nitrogen atoms.
They were fixed at 1.0Å from their parent N-atoms, but because the Ni-N-H angle is less than a regular tetrahedral angle, they could not be placed in calculated positions. Modelled as free atoms, not all of these hydrogens refined successfully, and two had to be fixed in the positions they were originally located in (H122 and H222). At the expense of 26 parameters an improvement

TABLE 3.5 DETERMINATION OF THE ABSOLUTE STRUCTURE

A	Structure as solved ($+x_j$) and refined with $+f''$	R = 0.0674 R_G = 0.0696 S = 2.94
B	Inverse of A ($-x_j$) refined with $+f''$	R = 0.0715 R_G = 0.0715 S = 3.12
	Conclusion: A is the correct structure	
C	Structure B ($-x_j$) refined with f'' = 0.0	R = 0.0682 R_G = 0.0711 S = 2.99
D	F_c calculated on C ($-x_j$) with $+f''$, no least-squares refinement	R = 0.0717 R_G = 0.0750 S = 3.15
E	F_c calculated on inverse of C ($+x_j$) with $+f''$, no least-squares refinement	R = 0.0677 R_G = 0.0707 S = 2.97

Hamilton's Test: Hypothesis - Structure D ($-x_j$) has the correct absolute configuration

$$R_{1,120,0.005} = 1.034$$

$$R_{1,2026,0.005} \simeq 1 + \frac{120}{2026}(1.034 - 1)$$

$$\simeq 1.002$$

$$R_{D/E} = 1.061$$

Conclusion: Hypothesis that structure with ($-x_j$) has the correct absolute configuration can be rejected at the 0.005 level.

in the generalized residual, R_G, from 0.0728 to 0.0609 was achieved. At a significance level of 0.005 the structure not containing the amine hydrogens could be discarded as the better model.

When a weighting scheme $w = 1/\sigma^2 F$ was introduced and the parameters were refined to shift$<1/50$esd , the final residual obtained was R = 0.0623, corresponding to a goodness-of-fit parameter S = 4.585. Fractional positional atomic parameters and temperature factors are listed in Table 3.6. Observed and calculated structure factors appear in Appendix 5.

iv) Description of the Structure

1) Molecular Structure

Perspective views of the two independent molecules showing atomic nomenclature appear in Fig.3.11. Symmetry-related ligands are indicated by their nitrogen atoms. Molecular bond lengths and bond angles are listed in Tables 3.7 and 3.8 respectively. Selected torsion angles appear in Table 3.9. The environments of the nickel atoms are shown in Fig. 3.12.

Molecule 1

The nickel atom is situated in a special position on a two-fold axis. Two isothiocyanate N-atoms in *cis* positions and four amine N-atoms are coordinated to the nickel, forming a slightly distorted octahedron. As in the $Ni(NCS)_2$(subst. pyridine)$_4$ molecules, the Ni-N distances for the isothiocyanates are smaller than for the amine ligands. The isothiocyanates deviate from linearity.

The remaining ligands are four (R)-α-phenylethylamine groups.

The Ni-N distances of these differ significantly: *viz.* 2.152(10)Å for the two amines *trans* to the isothiocyanate groups (but *cis* to each other), compared to 2.116(11)Å for the two symmetry-related amines in *trans* positions (N13 and N13', Fig.3.12a). This may be explained by the so-called 'trans-influence', which is the extent to which a ligand weakens the bond *trans* to itself in the equilibrium state of the complex[86].

Angles subtended at the nickel atom differ significantly from 90°, which may be a result of crowding of the $-NH_2-$ groups around the nickel atom. Looking down the two-fold axis (see Fig.3.14b), the four ligands extend from the nickel atom in a propeller-like conformation. The dihedral angle between the phenyl groups of adjacent amine ligands is 85.8°. The phenyl moieties are planar to within 0.04Å, but show some variation in their bond lengths (1.27(2)Å - 1.45(2)Å). The equation of the least-squares mean planes and respective atomic deviations are listed in Table 3.10.

Molecule 2

Once more the Ni-atom is situated on a two-fold axis, and its environment is essentially the same as in Molecule 1. In this case, however, the Ni2-N21-C2 angle is more greatly distorted (151.7°).

Two (R)-α-phenylethylamine ligands are *trans* to the isothiocyanate groups, while two (S)-αC amine ligands are situated *trans* to each other.

As can be seen by the comparison of the torsion angles in Table 3.9, a most remarkable similarity exists between the two molecules: the orientations of all atoms are very similar,

but in opposite direction is observed for the two-fold axes

at (x,y = 0.5). The stacking distances between two nickel atoms along these axes are 7.04 and 7.71Å alternately.

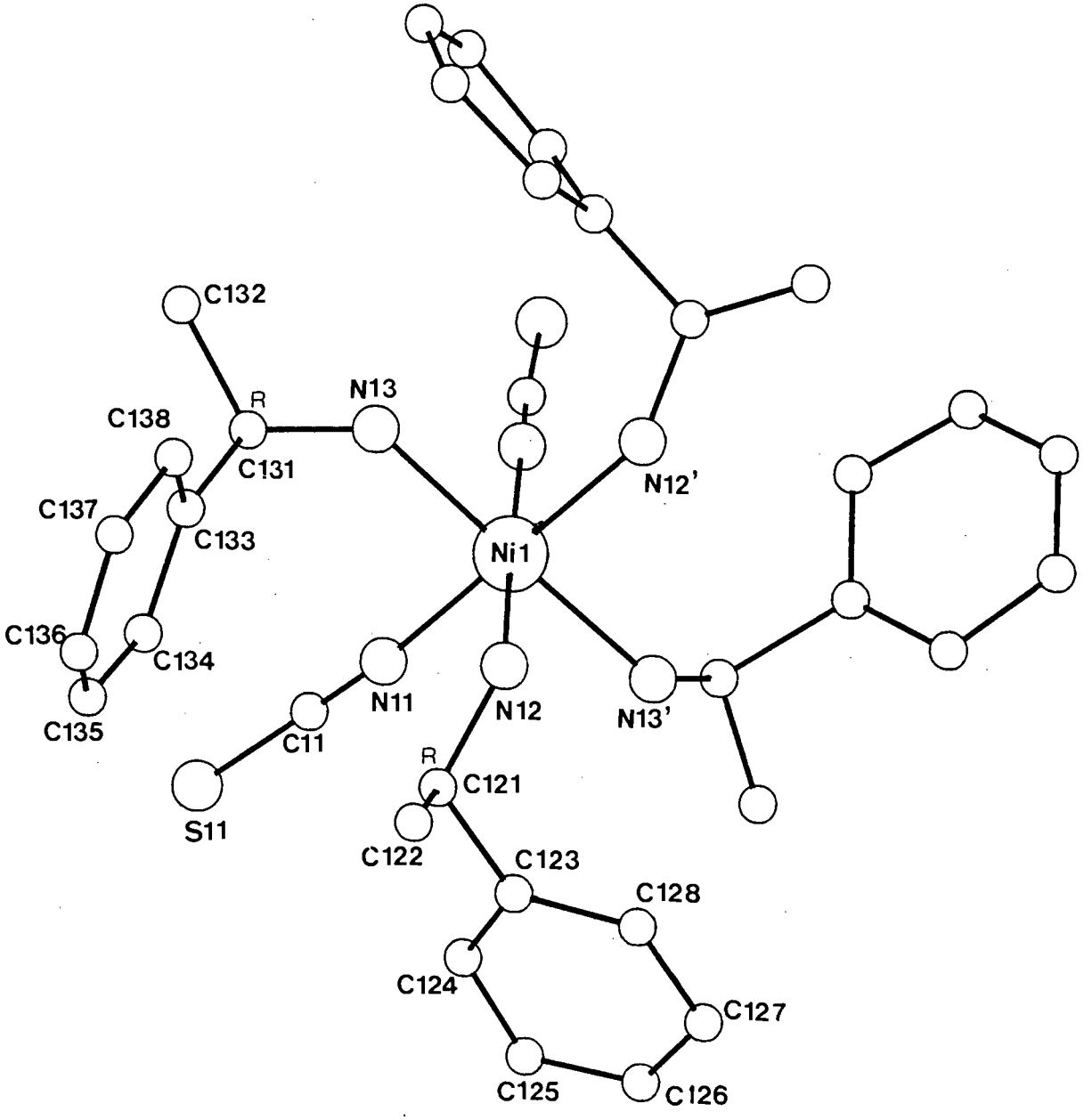


Figure 3.11a Perspective view of Molecule 1

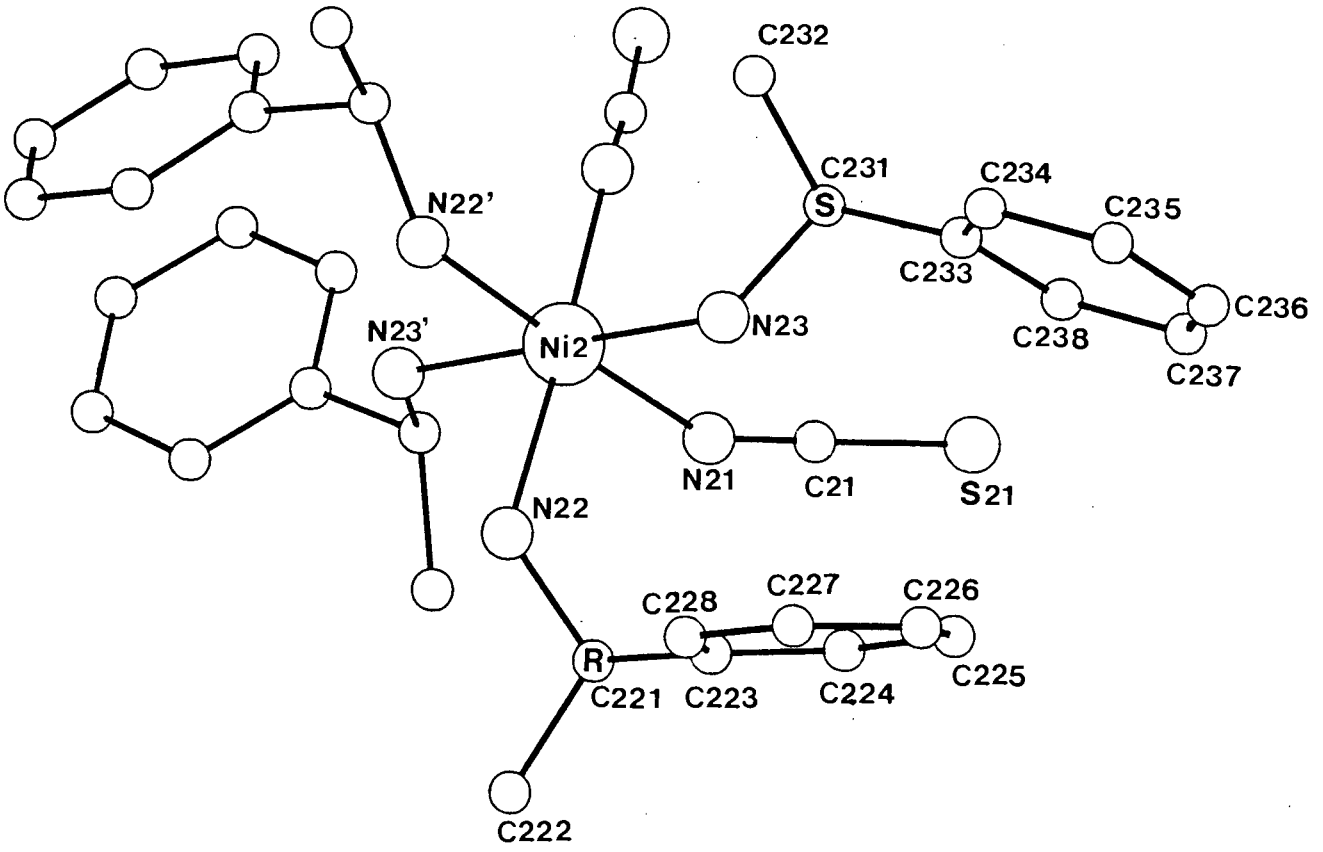
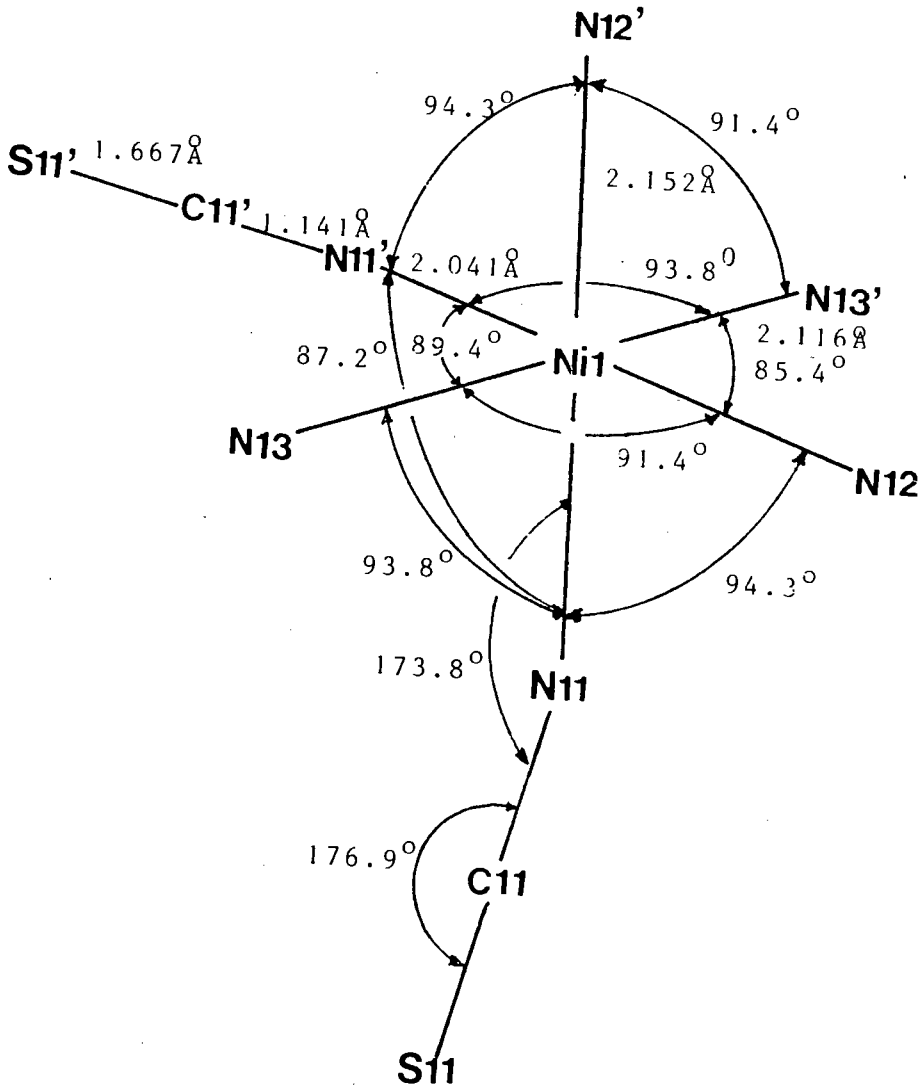


Figure 3.11b Perspective view of Molecule 2



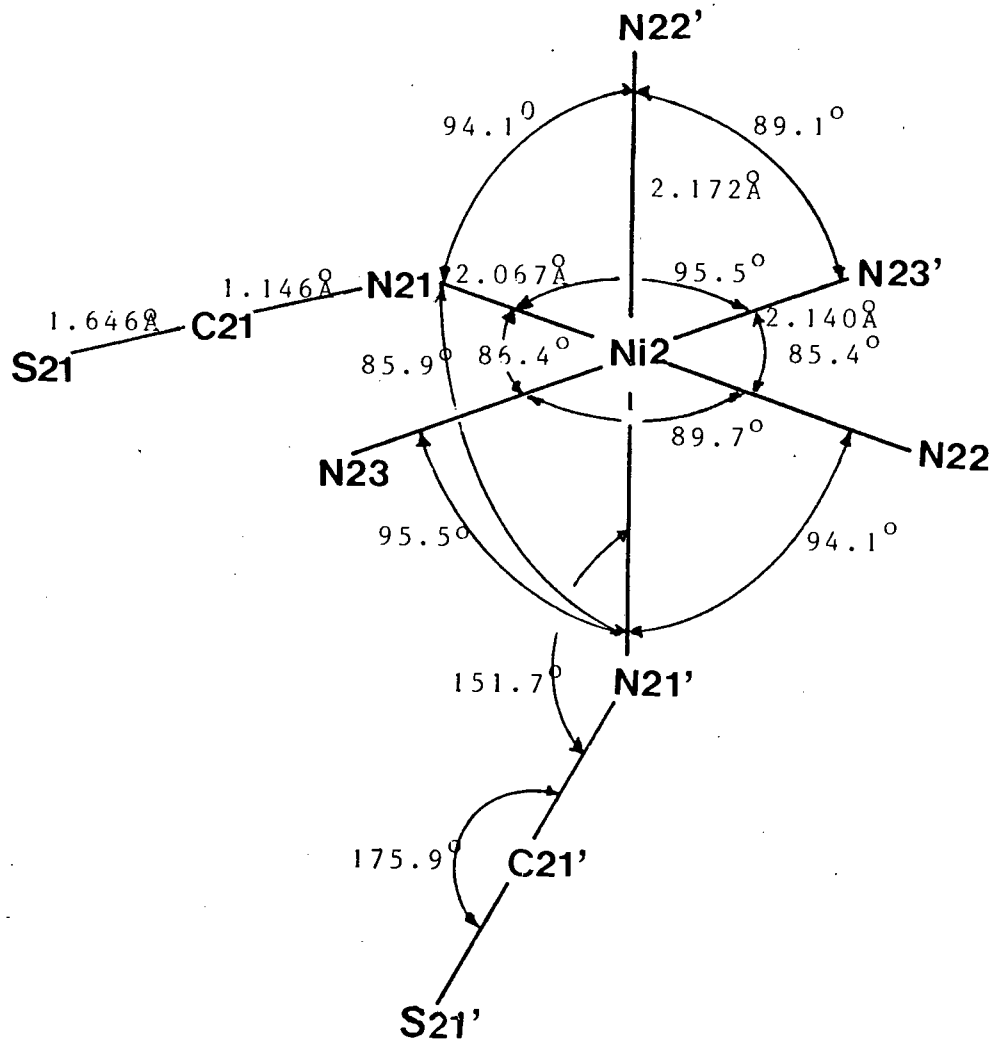


Figure 3.12 The environments of the nickel atoms, including the isothiocyanate ligands.

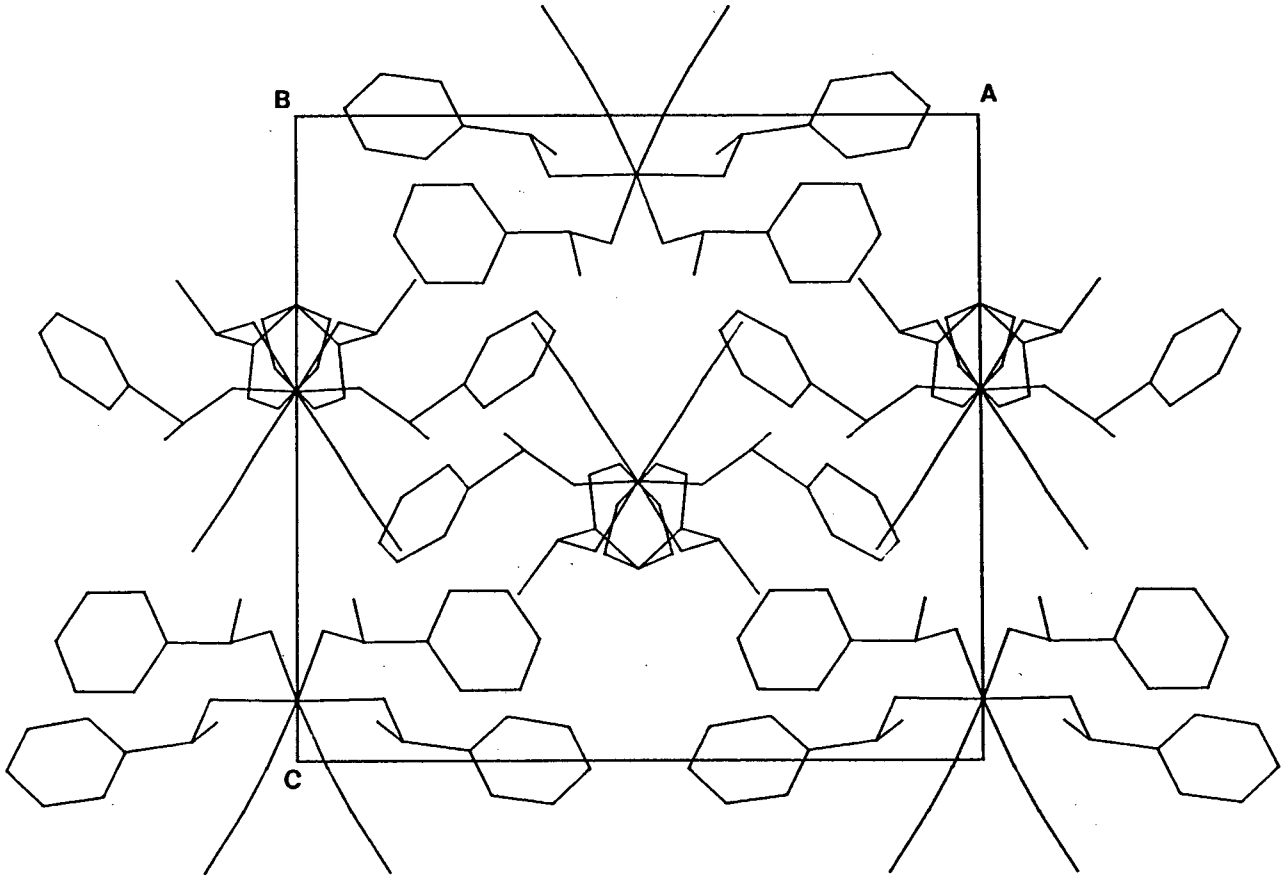


Figure 3.14a Packing of the molecules in the unit cell shown in projection down the y axis.

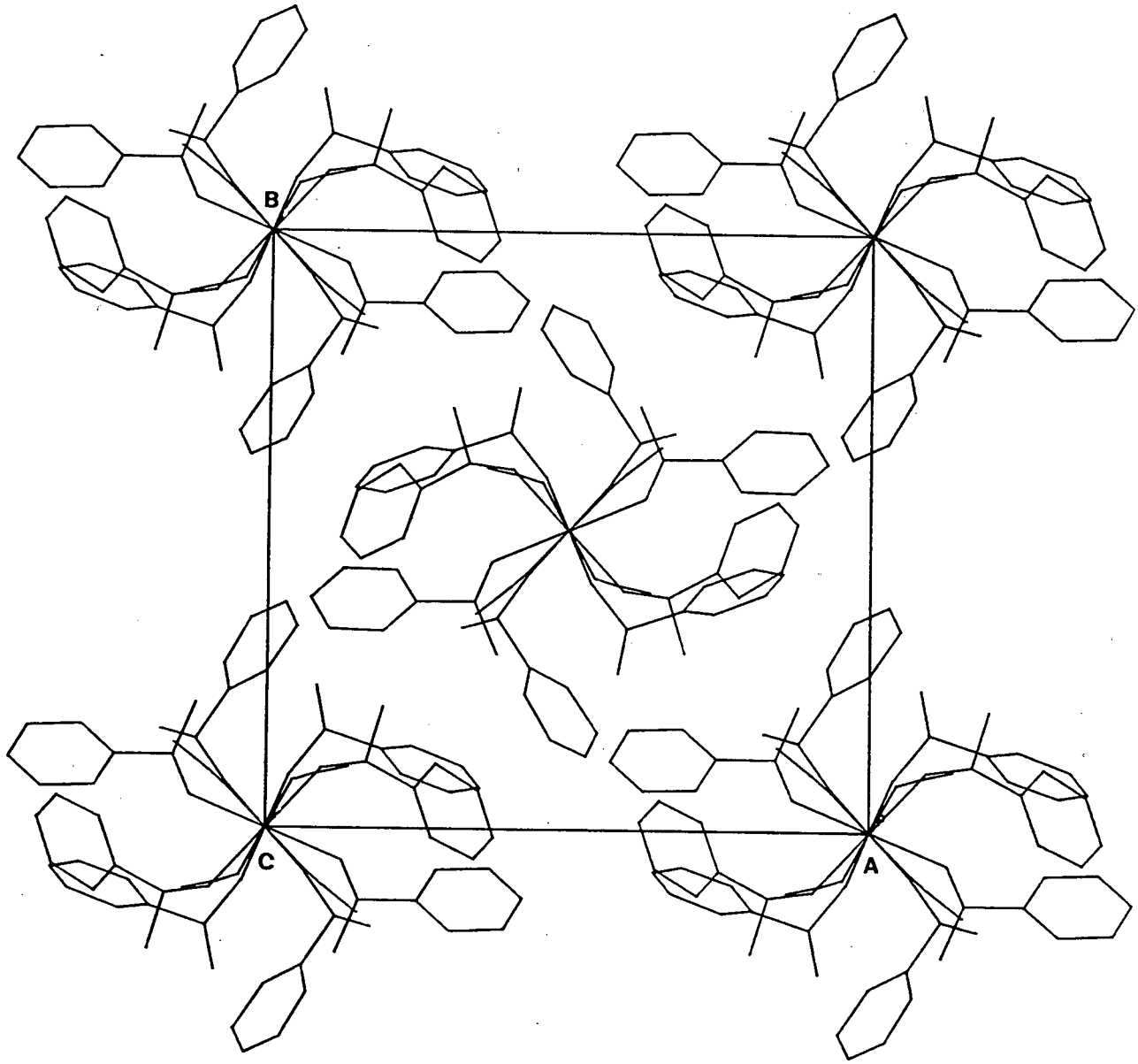


Figure 3.14b Packing of the tetramine molecules in the unit cell shown in projection down the *z* axis.

TABLE 3.6 FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS ($U_{ij} \times 10^3$)

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
Molecule 1				
Ni1	.5000	.5000	.5701(1)	a
N11	.4372(6)	.4337(6)	.4699(7)	61(3)
C11	.4024(6)	.4035(7)	.4094(8)	44(3)
S11	.3468(3)	.3592(3)	.3244(3)	a
N12	.4372(5)	.4305(6)	.6783(7)	49(3)
H121	.4787(28)	.4147(38)	.7269(27)	0(19)
H122	.3967(0)	.4646(0)	.7254(0)	109(44)
C121	.3823(7)	.3525(7)	.6610(10)	64(4)
H621	.3468(7)	.3644(7)	.6058(7)	122(25)
C122	.3244(8)	.3362(9)	.7436(10)	91(5)
H622	.2952(8)	.2805(9)	.7269(10)	78(11)
H623	.2801(8)	.3824(9)	.7538(10)	78(11)
H624	.3585(8)	.3264(9)	.8003(10)	78(11)
C123	.4371(7)	.2703(8)	.6440(9)	66(4)
C124	.4289(7)	.2257(8)	.5604(9)	71(4)
H124	.3905(7)	.2501(8)	.5123(9)	187(16)
C125	.4733(7)	.1494(8)	.5439(9)	74(4)
H125	.4631(7)	.1149(8)	.4874(9)	187(16)
C126	.5306(8)	.1228(9)	.6062(10)	83(5)
H126	.5619(8)	.0671(9)	.5930(10)	187(16)
C127	.5501(8)	.1626(9)	.6832(11)	93(5)
H127	.5975(8)	.1413(9)	.7233(11)	187(16)
C128	.4998(8)	.2376(7)	.7059(8)	71(3)
H128	.4913(8)	.7326(7)	.7655(8)	187(16)

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
N13	.4074(7)	.6012(7)	.5757(8)	66(3)
H131	.3890(52)	.6464(41)	.6205(42)	49(31)
H132	.4284(49)	.6365(49)	.5228(37)	57(32)
C131	.3338(9)	.6113(9)	.5214(10)	81(5)
H631	.2824(9)	.5737(9)	.5096(10)	122(25)
C132	.3059(8)	.7038(7)	.4966(10)	87(5)
H632	.2630(8)	.7165(7)	.4470(10)	78(11)
H633	.3654(8)	.7121(7)	.4722(10)	78(11)
H634	.2964(8)	.7446(7)	.5486(10)	78(11)
C133	.2532(8)	.5677(8)	.5803(10)	76(4)
C134	.2240(7)	.4843(8)	.5450(9)	77(4)
H134	.2400(7)	.4444(8)	.4941(9)	187(16)
C135	.1535(9)	.4495(9)	.5946(11)	101(5)
H135	.1431(9)	.3937(9)	.5611(11)	187(16)
C136	.1208(8)	.4859(8)	.6642(10)	91(4)
H136	.0728(8)	.4705(8)	.7065(10)	187(16)
C137	.1469(10)	.5647(10)	.6937(11)	110(6)
H137	.1086(10)	.5786(10)	.7462(11)	187(16)
C138	.2169(9)	.6087(9)	.6534(10)	97(5)
H138	.2270(9)	.6623(9)	.6906(10)	187(16)
Molecule 2				
Ni2	.5000	.5000	.0926(1)	a
N21	.5444(5)	.4198(6)	-.0100(7)	58(3)
C21	.5796(7)	.4089(8)	-.0773(8)	55(4)
S21	.6362(2)	.3967(2)	-.1798(3)	a
N22	.4618(7)	.5889(7)	.2001(7)	54(3)
H221	.5220(25)	.6031(66)	.2192(68)	92(45)
H222	.4191(0)	.5457(0)	.2018(0)	207(74)
C221	.4023(7)	.6637(7)	.1824(9)	57(3)
H721	.4148(7)	.6871(7)	.1205(9)	122(25)

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
C222	.4168(8)	.7381(7)	.2489(9)	74(4)
H722	.4746(8)	.7617(7)	.2319(9)	78(11)
H723	.4150(8)	.7272(7)	.3157(9)	78(11)
H724	.3714(8)	.7815(7)	.2323(9)	78(11)
C223	.3093(6)	.6325(7)	.1840(8)	50(3)
C224	.2595(7)	.6378(8)	.1075(9)	71(4)
H224	.2831(7)	.6648(8)	.0510(9)	187(16)
C225	.1734(8)	.6042(8)	.1090(10)	79(4)
H225	.1362(8)	.6069(8)	.0538(10)	187(16)
C226	.1441(8)	.5689(8)	.1868(9)	76(4)
H226	.0832(8)	.5478(8)	.1886(9)	187(16)
C227	.1913(8)	.5606(8)	.2608(10)	89(5)
H227	.1665(8)	.5324(8)	.3161(10)	187(16)
C228	.2748(7)	.5909(8)	.2617(9)	67(4)
H228	.3111(7)	.5836(8)	.3172(9)	187(16)
N23	.6270(6)	.5540(6)	.0958(7)	47(2)
H231	.6556(44)	.4987(28)	.0763(54)	55(26)
H232	.6463(75)	.5814(74)	.1537(45)	138(54)
C231	.6555(8)	.6205(8)	.0293(10)	73(4)
H731	.6330(8)	.6062(8)	-.0325(10)	122(25)
C232	.6183(9)	.7081(7)	.0599(11)	98(5)
H732	.6439(9)	.7329(7)	.0033(11)	78(11)
H733	.6379(9)	.7431(7)	.1134(11)	78(11)
H734	.5541(9)	.7104(7)	.0558(11)	78(11)
C233	.7531(7)	.6210(7)	.0151(8)	55(3)
C234	.7855(7)	.5688(7)	-.0531(9)	66(4)
H234	.7461(7)	.5338(7)	-.0925(9)	187(16)
C235	.8741(8)	.5660(8)	-.0658(10)	89(5)
H235	.8985(8)	.5279(8)	-.1145(10)	187(16)

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
C236	.9283(8)	.6147(8)	-.0127(9)	70(4)
H236	.9919(8)	.6107(8)	-.0223(9)	187(16)
C237	.8976(8)	.6667(8)	.0512(10)	78(4)
H237	.9378(8)	.7035(8)	.0879(10)	187(16)
C238	.8084(7)	.6703(8)	.0673(9)	73(4)
H238	.7851(7)	.7085(8)	.1166(9)	187(16)

---

a

Anisotropic thermal parameters ($U_{ij} \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni1	39(1)	42(1)	52(1)	0	0	-4(1)
S11	93(3)	104(3)	53(2)	-5(3)	-5(3)	37(2)
Ni2	45(1)	47(1)	39(1)	0(0)	0(0)	9(1)
S21	93(3)	74(2)	45(2)	-5(2)	7(3)	7(2)

TABLE 3.7 BOND DISTANCES (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Molecule 1			*Molecule 2*		
Ni1 - N11	2.041(10)		Ni2 - N21	2.067(10)	
Ni1 - N12	2.152(10)		Ni2 - N22	2.172(11)	
Ni1 - N13	2.116(11)		Ni2 - N23	2.140(9)	
N11 - C11	1.141(15)		N21 - C21	1.146(15)	
C11 - S11	1.667(12)		C21 - S21	1.646(13)	
N12 - C121	1.489(14)		N22 - C221	1.494(15)	
C121 - C122	1.535(20)		C221 - C222	1.519(17)	
C121 - C123	1.540(16)		C221 - C223	1.523(14)	
C123 - C124	1.415(19)		C223 - C224	1.371(17)	
C124 - C125	1.378(17)		C224 - C225	1.434(17)	
C125 - C126	1.343(18)		C225 - C226	1.347(19)	
C126 - C127	1.324(21)		C226 - C227	1.321(19)	
C127 - C128	1.428(18)		C227 - C228	1.378(17)	
C128 - C123	1.426(17)		C228 - C223	1.416(17)	
N13 - C131	1.405(18)		N23 - C231	1.481(17)	
C131 - C132	1.525(18)		C231 - C232	1.528(17)	
C131 - C133	1.665(19)		C231 - C233	1.531(17)	
C133 - C134	1.451(18)		C233 - C234	1.380(17)	
C134 - C135	1.421(19)		C234 - C235	1.390(17)	
C135 - C136	1.274(21)		C235 - C236	1.370(18)	
C136 - C137	1.344(20)		C236 - C237	1.322(19)	
C137 - C138	1.411(21)		C237 - C238	1.408(17)	
C138 - C133	1.369(20)		C238 - C233	1.379(17)	

All C - H bond lengths[a] 1.00 Å

[a]Bond lengths fixed

TABLE 3.8 BOND ANGLES (DEGREES) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Molecule 1	
N11 - Ni1 - N13	93.8(.6)
N12 - Ni1 - N13	91.4(.5)
N11 - Ni1 - N12	94.3(.5)
N11 - C11 - S11	176.9(1.2)
Ni1 - N11 - C11	173.8(1.1)
Ni1 - N12 - C121	121.9(1.0)
N12 - C121 - C122	109.3(1.1)
N12 - C121 - C123	111.4(1.0)
C122 - C121 - C123	108.7(1.1)
C121 - C123 - C124	119.1(1.2)
C121 - C123 - C128	124.1(1.3)
C124 - C123 - C128	116.8(1.2)
C123 - C124 - C125	121.2(1.3)
C124 - C125 - C126	117.9(1.4)
C125 - C126 - C127	126.8(1.5)
C126 - C127 - C128	116.4(1.4)
C127 - C128 - C123	120.4(1.3)
Ni1 - N13 - C131	127.8(1.0)
N13 - C131 - C132	118.1(1.3)
N13 - C131 - C133	105.8(1.2)
C132 - C131 - C133	106.5(1.2)
C131 - C133 - C134	113.6(1.2)
C131 - C133 - C138	122.5(1.3)
C134 - C133 - C138	123.8(1.3)
C133 - C134 - C135	112.7(1.3)
C134 - C135 - C136	124.0(1.5)

C135 - C136 - C137	122.2(1.6)
C136 - C137 - C138	121.6(1.6)
Molecule 2	
N22 - Ni2 - N23	89.7(.5)
N21 - Ni2 - N22	176.1(.6)
N21 - Ni2 - N23	86.4(.5)
N21 - C21 - S21	175.9(1.3)
Ni2 - N21 - C21	151.7(1.1)
Ni2 - N22 - C221	121.4(.9)
N22 - C221 - C222	111.7(1.1)
N22 - C221 - C223	110.2(1.1)
C222 - C221 - C223	111.5(1.1)
C221 - C223 - C224	120.3(1.2)
C221 - C223 - C228	120.9(1.1)
C224 - C223 - C228	118.6(1.2)
C223 - C224 - C225	119.6(1.3)
C224 - C225 - C226	118.2(1.4)
C225 - C226 - C227	123.7(1.4)
C226 - C227 - C228	119.9(1.5)
C227 - C228 - C223	120.0(1.3)
Ni2 - N23 - C231	121.8(.9)
N23 - C231 - C232	107.1(1.2)
N23 - C231 - C233	113.0(1.2)
C232 - C231 - C233	114.3(1.2)
C231 - C233 - C234	117.4(1.2)
C231 - C233 - C238	123.0(1.2)
C234 - C233 - C238	119.8(1.2)
C233 - C234 - C235	118.5(1.2)
C234 - C235 - C236	121.0(1.4)
C235 - C236 - C237	120.8(1.4)
C236 - C237 - C238	119.9(1.4)
C237 - C238 - C233	119.9(1.3)

TABLE 3.9 SELECTED TORSION ANGLES

Molecule 1	*Angle*	*E.S.D.*
Ni1 - N12 - C121 - C122 *(R)*	-166.61°	(.93)
Ni1 - N12 - C121 - C123	78.21°	(1.29)
N12 - C121 - C123 - C124	-120.25°	(1.34)
Ni1 - N13 - C131 - C132 *(R)*	-145.56°	(1.15)
Ni1 - N13 - C131 - C133	95.50°	(1.35)
N13 - C131 - C133 - C134	-106.72°	(1.42)
Molecule 2		
Ni2 - N22 - C221 - C222 *(R)*	-153.13°	(1.37)
Ni2 - N22 - C221 - C223	82.45°	(.95)
N22 - C221 - C223 - C224	-116.74°	(1.37)
Ni2 - N23 - C231 - C232 *(S)*	78.74°	(1.32)
Ni2 - N23 - C231 - C233	-154.58°	(.94)
N23 - C231 - C233 - C234	-91.07°	(1.51)

TABLE 3.10 WEIGHTED LEAST-SQUARES PLANES

Equations of least-squares planes are expressed in orthogonal space as: M1×X + M2×Y + M3×Z = D

Molecule 1

Plane 1 : The phenyl group C123, C124, C125, C126, C127, C128

M1 = .7050(44)

M2 = .5605(53)

M3 = -.4345(56)

D = 3.0036(736)

Sum of $(D/S)^2$ for the atoms in this ring = 23.89

Chi-squared at 95% for 3 degrees of freedom = 7.81

The group of atoms deviates significantly from planarity.

Atom	*D*	*S*	*D/S*	$(D/S)^2$
C123	-.0226	.0137	-1.649	2.719
C124	.0408	.0137	2.981	8.886
C125	-.0212	.0137	-1.552	2.407
C126	-.0207	.0150	-1.375	1.891
C127	.0409	.0153	2.674	7.148
C128	-.0126	.0137	-.918	.843
				23.894

Plane 2 : The phenyl group C133, C134, C135, C136, C137, C138

M1 = -.6426(51)

M2 = .4691(62)

M3 = -.6058(54)

D = -3.6321(851)

Sum of $(D/S)^2$ for atoms in this ring = 4.211

Chi-squared at 95% for 3 degrees of freedom = 7.81

The group of atoms does not deviate significantly from planarity.

Dihedral angle formed by LSQ-planes 1 - 2 : 85.81(.41)°

Molecule 2

Plane 3 : The phenyl group C223, C224, C225, C226, C227, C228

M1 = .3325(55)

M2 = -.8903(26)

M3 = -.3113(57)

D = -7.8461(386)

Sum of (D/S) for the atoms in this ring = 4.964

Chi-squared at 95% for 3 degrees of freedom = 7.81

The group of atoms does not deviate significantly from planarity.

Plane 4 : The phenyl group C233, C234, C235, C236, C237, C238

M1 = -.0723(55)

M2 = .7551(36)

M3 = -.6517(42)

D = 6.1901(784)

Sum of (D/S) for the atoms in this ring = 1.733

Chi-squared at 95% for 3 degrees of freedom = 7.81

The group of atoms does not deviate significantly from planarity.

Dihedral angle formed by LSQ-planes 3 - 4 : 119.56(.42)

b) The Crystal and Molecular Structure of 1:1 $[Ni(NCS)_2((R)$-α-phenylethylamine$)_2((S)$-α-phenylethylamine$)_2]$: *sec*-Butylbenzene

i) Intensity Data Collection

The monoclinic crystal system was determined by indexing reflections found by the automatic peak search routine of the diffractometer. A trial data set revealed C-centering and thus data except *(hkl): h+k=2n+1* were collected in the θ-range $1^o<\theta<25^o$. The intensities of three standard reflections which were periodically monitored were stable to within 1,7% of their mean values. Data were L.p. processed and an absorption correction was applied, giving minimum and maximum transmissions as 89.28 and 99.95% respectively. Accurate cell parameters were determined by least-squares analysis of 25 reflections in the θ-range $10^o<\theta<11^o$; again, the low intensity of higher-order reflections precluded their use in the cell refinement procedure. Together with other relevant crystal data they are listed in Table 3.11.

ii) Solution and Refinement of the Structure

Inspection of the intensity data revealed systematic absences, in addition to the *(hkl): h+k=2n* condition of non-extinction for the C-centered cell. These absences conform to the following rules of non-extinction:

$$(h0l): \quad (h=2n),\ l = 2n$$
$$(0k0): \quad k = 2n$$

They are indicative of the space-group Cc (No.9) and $C_{2/c}$ (No.15),

TABLE 3.11 CRYSTAL DATA

Molecular formula	$C_{34}H_{44}N_6NiS_2:C_{10}H_{14}$
Molecular weight	$794.71 gmol^{-1}$
Space-Group	C2/c
a	10.716(10)Å
b	30.604(6)Å
c	13.685(29)Å
α	90.0°
β	97.74(14)°
γ	90.0°
Volume	$4447(10)Å^3$
Z	4
D_c	$1.19 gcm^{-3}$
$\mu(MoK_\alpha)$	$4.73 mm^{-1}$
F(000)	1474
Crystal Dimensions	0.25 x 0.19 x 0.19mm
Scan mode	ω-2θ
Scan width	$(0.78+0.35\tan\theta)^\circ$
Vertical aperture length	4mm
Aperture width	(1.11+1.05tanθ)mm
Final acceptance limit	20σ at $20^\circ min^{-1}$ in ω
Maximum recording time	40s
Crystal stability	1.7%
Range scanned	$1 - 25^\circ\theta$
Total number of reflections	4188
Final Refinement Data	
R	0.095
R_w	0.079
S	3.34
N	1395
NP	137

the latter being the centrosymmetric equivalent of the former.

Although no weak reflections were measured the mean $|E^2-1|$ statistics, calculated on 2573 unique reflections, indicated a centrosymmetric cell. With Z=4, the nickel atoms would have to fall on a special position in the centric space-group (number of general positions = 8), which would coincide with a general position of the space-group Cc. Therefore the expected Patterson map for the NixNi vectors would be identical for both space-groups, and could not be used to determine whether the structure is centric or not, as has been done elsewhere[87]. Consequently the structure was solved in the centrosymmetric space-group, and successful refinement vindicated this choice. In addition, an attempt to solve the structure in the space-group Cc resulted in extensive correlation in the L.S. matrix, substantiating that the structure is centrosymmetric.

From the Patterson map the nickel atoms were located at the special position (0.25, 0.25, 0.50) (Wykhoff position *d*). An electron density map based only on the nickel atoms (R=0.48) revealed seventeen non-hydrogen atoms, constituting almost the entire host molecule. When all non-H atoms of the host molecule were inserted and the Ni-atom treated anisotropically (no β-restrictions apply as the site symmetry is only $\bar{1}$), the conventional R-value was 0.17.

There now remained seven peaks of electron density which were independent of the nickel complex. Three of these were located on special positions (0.0, y, 0.25) (Wykhoff position *e*), which has a two-fold axis for its site-symmetry. Although the *sec*-butylbenzene molecule does not have a two-fold axis, the

major part of the molecule can be accommodated in this position (Fig. 3.15).

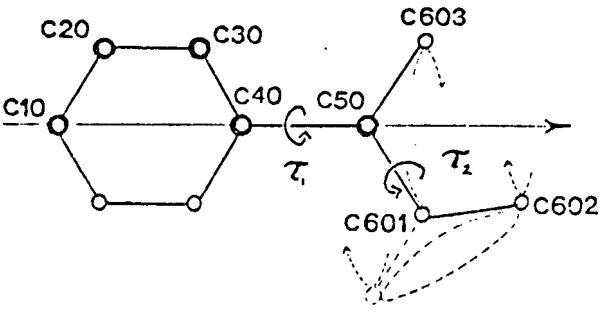
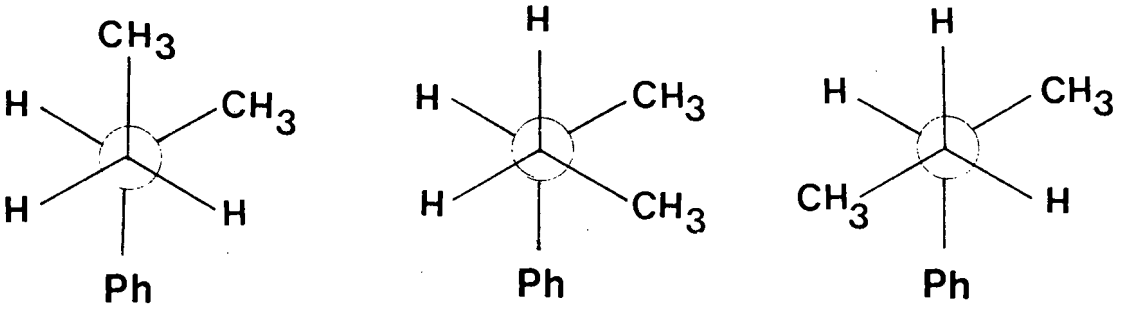


Figure 3.15 *Sec*-Butylbenzene molecule: atoms compatible with 2-fold axis are drawn in heavy lines.

When these atoms were included in the model (C10, C40, C50; all at s.o.f.=0.5 and C20, C30 at s.o.f.=1.0), the conventional residual dropped to R=0.12. As the remainder of the guest molecule stems from a tetrahedral carbon atom (C50 above), it has to be disordered. Electron density maps were drawn to determine the entire conformation of the guest molecules. Figure 3.17a depicts electron density maps in the *yz* plane along the two-fold axis where the guest compound appears. (Only half of the molecule is shown.) From this the disordered butyl group is seen to give rise to a disk of electron density. Of the most likely conformers of the guest compound to have been enclathrated, the one depicted in Fig. 3.16a could therefore be ruled out.



(a) (b) (c)

Fig. 3.16 Staggered conformations of *sec*-butylbenzene, rotation about τ_2 (Fig. 3.15)

The electron density was now mapped in the *xz* plane (Fig.3.17b). The map contains a two-fold axis and from a symmetry-point of view is able to accommodate one enantiomer of the guest compound better than the other[¶]. However, the shape of the area of disordered electron density cannot be explained by the presence of just one enantiomer in this particular guest-site. The way in which the butyl groups of both enantiomers have been fitted to the map is depicted in Fig. 3.17b.

Figure 3.17(a) Electron density map of guest-site:*yz* plane

Figure 3.17(b) Electron density map of guest-site:*xz* plane

[¶]*An inversion-center-related guest site would then accommodate preferentially the other enantiomer!*

Approximate coordinates for each of the two enantiomers were taken from these electron density maps. In both cases they correspond to the staggered conformation as in Fig. 3.16c. The energy-minimization facility of the program EENY was then used to improve the approximate values before they were used in subsequent L.S. refinement.

When hydrogen atoms of the host molecule (except $-N\underline{H}_2-$ hydrogens) were inserted in calculated positions, the Ni and S atoms treated anisotropically and the enantiomerically- aswell as rotation-disordered guest was included in the refinement, an R-value of 0.11 was achieved. Thermal parameters of the atoms constituting the disordered part of the guest molecule were linked together.
Some thermal parameters of positional hydrogens, however, were very high (0.23), and were subsequently fixed to 1.2 times the value of the thermal parameters of their respective parent carbon atoms. Finally, when a weighting scheme $1/\sigma^2 F$ was applied, a weighted residual, $R_w = 0.078$ was obtained, and a goodness-of-fit parameter $S = 3.34$.

The final fractional positional atomic parameters with corresponding thermal motion parameters are listed in Table 3.12. Observed and calculated structure factors are listed in Appendix 6.

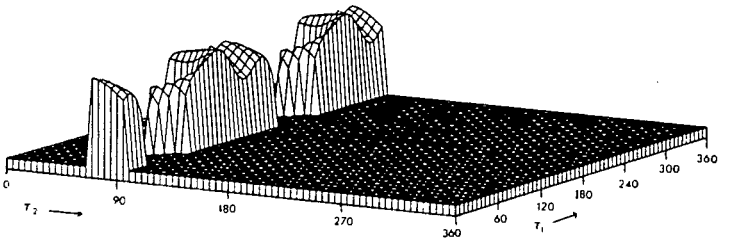
iii) An Energy Study of the Conformational Freedom of the Guest Molecules

To confirm that both enantiomers of *sec*-butylbenzene can be accommodated by each guest-site and to determine any other possible low-energy conformations of the guest molecules other

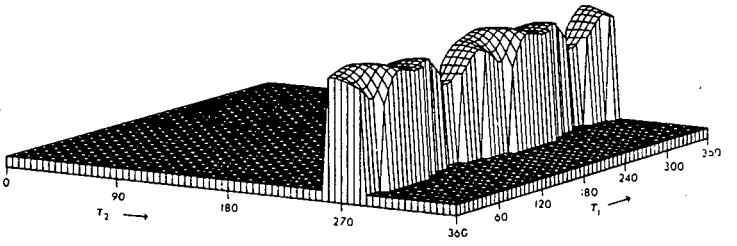
than those indicated by the electron density, a potential energy study of the guest in the host lattice was performed. The P.E. program EENY was used to map the molecular potential energies of the guest molecule in terms of two torsion angles, τ_1 and τ_2 (see Fig.3.15).
Interactions for all molecules within a range of 6Å from the guest molecule in every direction were considered. The approximate coordinates of the disordered butyl-groups of both enantiomers obtained above were used to describe bond-lengths and -angles. The values of τ_1 were stepped through the range 0° - 360° in intervals of 6°, those of τ_2 at intervals of 5° through the same range. The results are shown in Fig. 3.18.

The energy minima for both enantiomers were approximately the same (-27 and -33kcal/mol); the difference may be ascribed to the use of approximate and not exact enantiomeric input coordinates. The similarity implies that the probability of finding either of the two enantiomers in every guest-site is the same.

It can be seen that values of τ_2 giving rise to structures with negative calculated intermolecular energies are severely limited. The disk shape of the disordered butyl group as seen in electron density maps, is confirmed.
Compared to energy minima of ≈30kcal/mol in the low-energy regions depicted in Fig. 3.18, which correspond to the molecular conformation shown in Fig. 3.16c, the absence of any other negative values for the alternate staggered conformation ($\tau_1 + 120^\circ$), which would also give rise to a disk-shaped butyl-group (Fig. 3.16b), confirms that the guest molecules are enclathrated in only one conformation, and that the guest molecules in the structure refinement above are an adequate model of the observed electron density.



(a) Low-energy profile for *sec*-butylbenzene conformations in the clathrate (green enantiomer, Fig.3.17b).



(b) Low-energy profile for *sec*-butylbenzene conformations in the clathrate (orange enantiomer, Fig.3.17b).

Figure 3.18 Energy profiles of the two enantiomers in the clathrate structure. The conformations are expressed in terms of two torsion angles, τ_1 and τ_2 (Fig.3.15).

iv) Description of the Crystal Structure

1) Molecular Structure

A perspective view of the host complex is shown in Fig. 3.19. bond lengths and angles are listed in Tables 3.13 and 3.14 respectively. Selected torsion angles appear in Table 3.15, and weighted least-squares planes of the phenyl groups in Table 3.16.

Most significantly, in this clathrate the isothiocyanate groups of the Ni-complex are in *trans*-positions, allowing the nickel atom to fall on an inversion center. It follows that two (*d*)- and two (*l*)-α-phenylethylamine ligands respectively are *cis* to each other, as the inversion center produces a ligand of opposite chirality in the *trans* position.

As observed in all Werner nickel complexes with isothiocyanate groups, their Ni-NCS distances are significantly different from the Ni-N distances for the other amine ligands. Because the nickel atom lies on a center of inversion, it is coplanar with any two pairs of symmetry-related coordinated nitrogens. These nitrogens form a distorted octahedron. The distortion may be due to molecular packing. The N-Ni-N angles for the octants facing the sulphur atom of an adjacent molecule all exceed 90°. The environment of the nickel atom is depicted in Fig. 3.20.

Two (*d*)- and two (*l*)-α-phenylethylamine ligands are coordinated in a plane around the nickel atom. The conformation of the amine nitrogens direct the α-C atoms alternately almost as far as possible above and below the plane containing the four amine nitrogens. (The torsion angles N1-Ni-N2-C21 and

N1-Ni-N3-C31 are 11.5 and 9.2° respectively.)

The planes of the phenyl groups of the amine ligands form a dihedral angle of 21.5°. The distance between the two phenyl groups of two amine ligands having their α-C atoms pointing in opposite directions out of the amine-N plane is small enough to suggest that there is some π-π interaction of the two aromatic rings. The equation of Plane 1 in Table 3.15 was used to determine the distances of C33 (3.18Å) and C36 (2.56Å) from that plane using the formula

$$d = \frac{M1x_o + M2y_o + M3z_o + D}{\pm\sqrt{M1^2 + M2^2 + M3^2}}$$

where (x_o, y_o, z_o) are the orthogonal coordinates of the two atoms C33 and C36 respectively. The shortest interatomic distance between the phenyl groups is C27 - C34 (3.46Å).

Bond distances in the phenyl groups of the amine ligands vary between 1.32Å and 1.45Å. The atoms constituting these phenyl rings, except C23 and C33, also have the highest thermal parameters of all nickel-complex atoms. This may be caused by some small non-centrosymmetric displacements. As the phenyl groups are also close to the disordered guest molecules, their environment may also be somewhat affected depending on which real enantiomer is situated in an adjacent cavity.

2) Packing

Illustrations of the molecular packing in projection along (100) (Fig.3.21a) and (001) (Fig.3.21b), aswell as a packing diagram along (010) (Fig.3.21c) are shown. For clarity, only one guest molecule is included in the last of these.

The structure consists of discrete, centrosymmetric nickel-complex molecules and asymmetric guest molecules. The host-molecules form a grid of closely packed layers in the (400) planes. The isothiocyanate groups lie parallel to these planes, the sulphur atoms approaching the expanded octants of an adjacent complex (i.e. those for which N-Ni-N>90°, mentioned earlier).

The phenyl groups of the amine ligands all point towards the (020) planes, forming cavities around two-fold axes which are occupied by the guest molecules. As both the nickel-complex and guest molecules are situated on centers of symmetry with equal multiplicity, the maximum value for the molar host:guest ratio is 1:1.

The phenyl planes of guest *sec*-butylbenzene molecules and host α-phenylethylamine ligands are not parallel as expected by Hanotier *et al*[42]. The hypothesis of charge-transfer guest to host interactions is therefore not supported by the crystal structure. The near-orthogonal relative orientations of the host-ligand and guest phenyl groups indicates instead that some repulsion between the π-electron clouds may be causing them to turn away from each other.

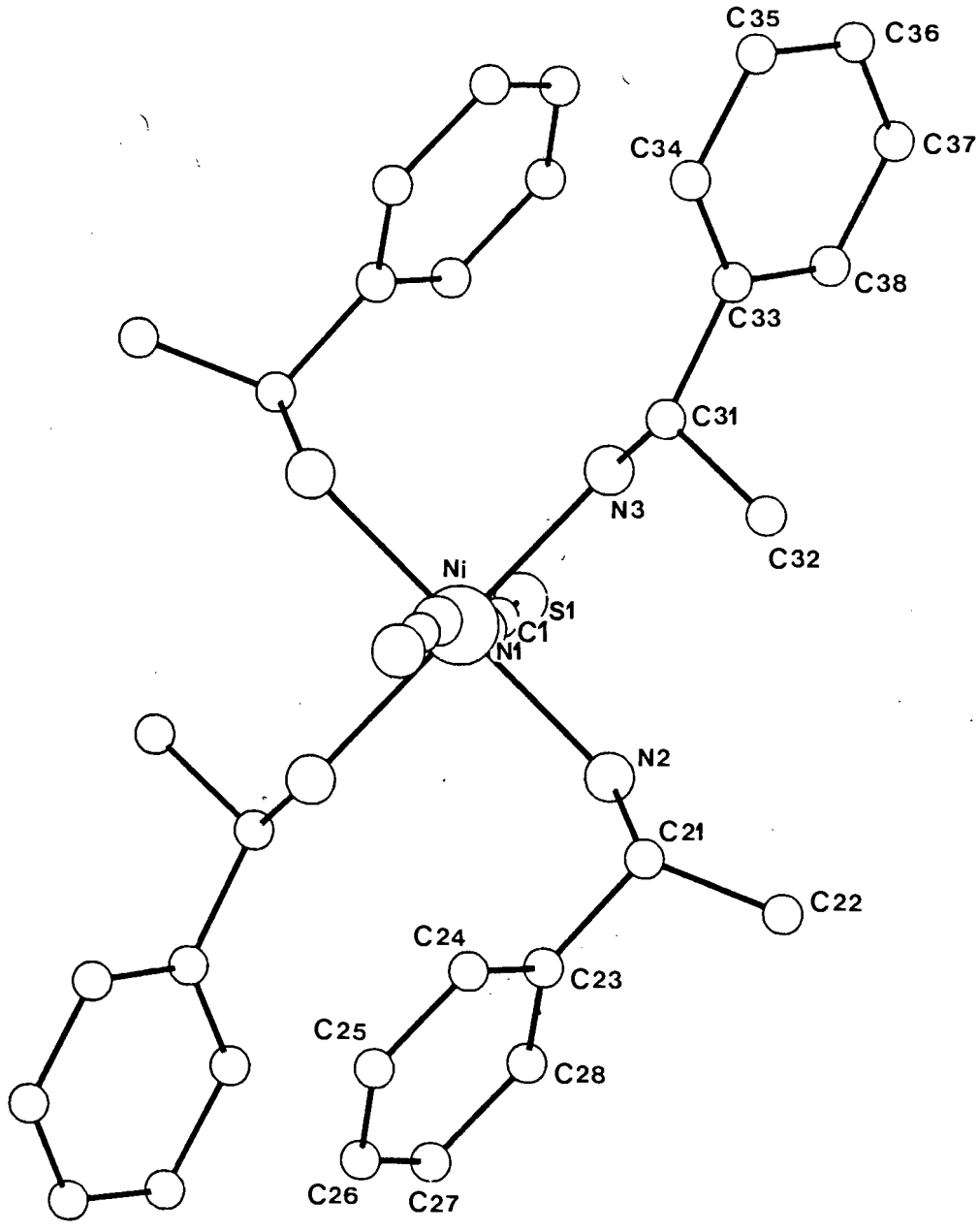


Figure 3.19 Perspective view of the *trans* nickel complex.

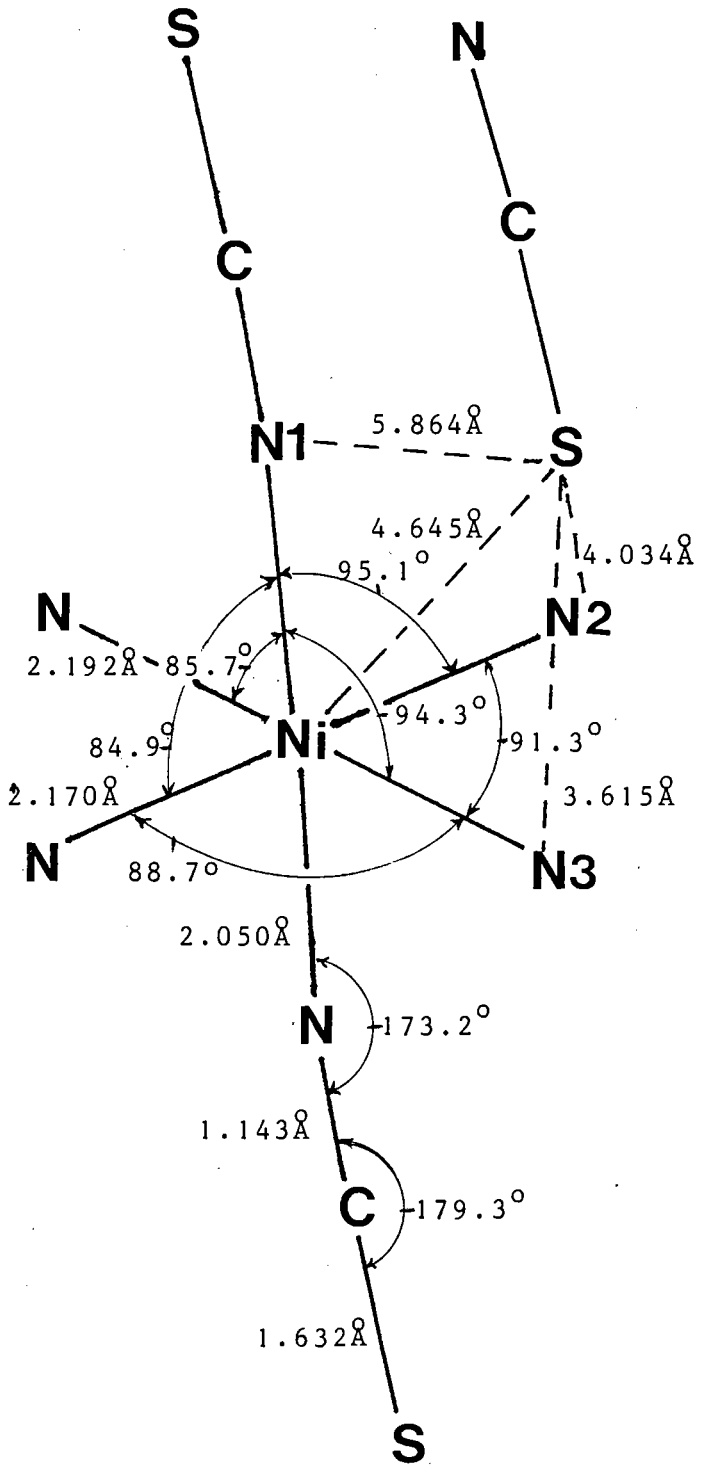


Figure 3.20 The environment of the nickel atom, including the *trans*-isothiocyanates

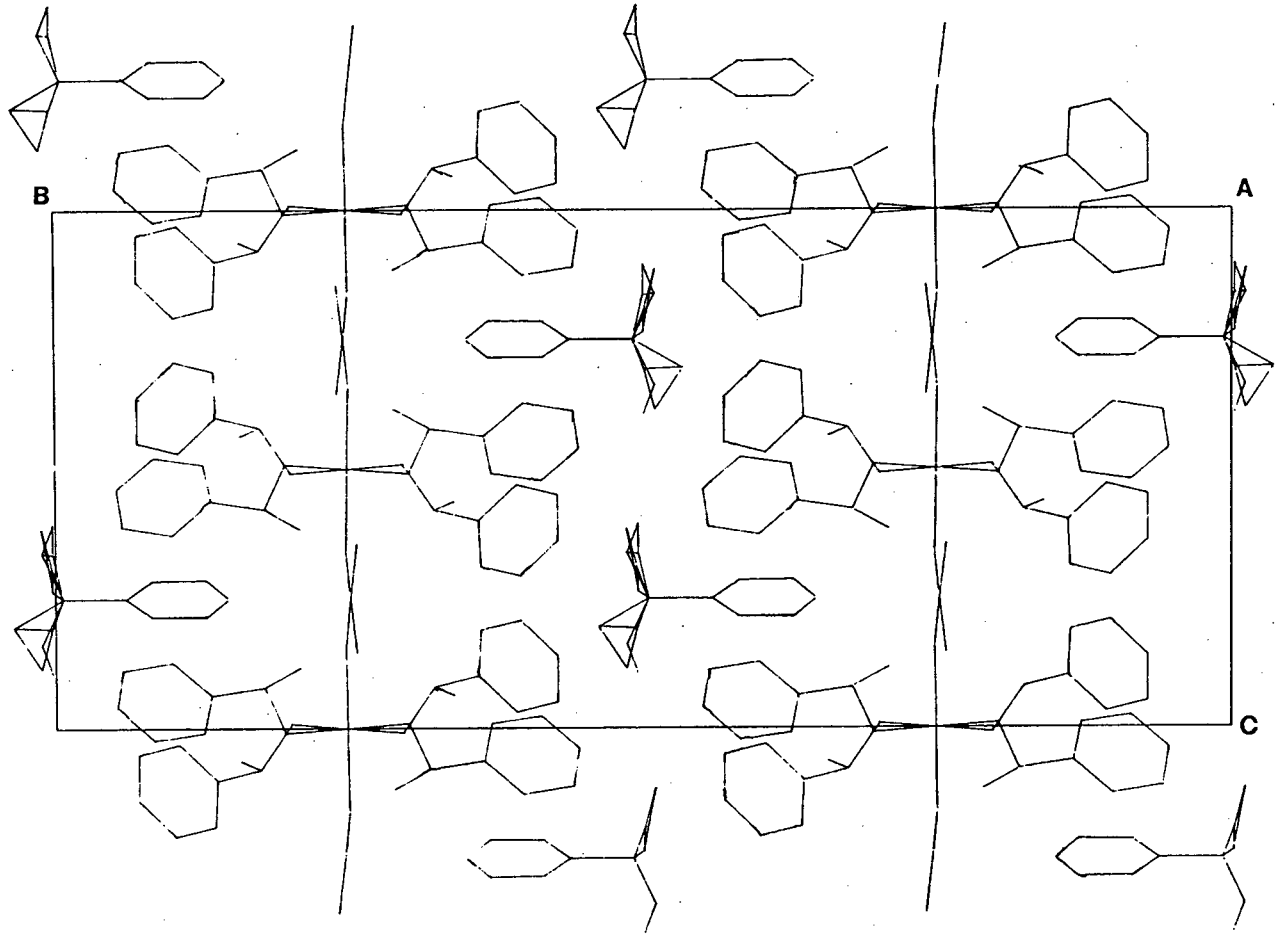


Figure 3.21 (a) An illustration of molecular packing viewed down the x axis.

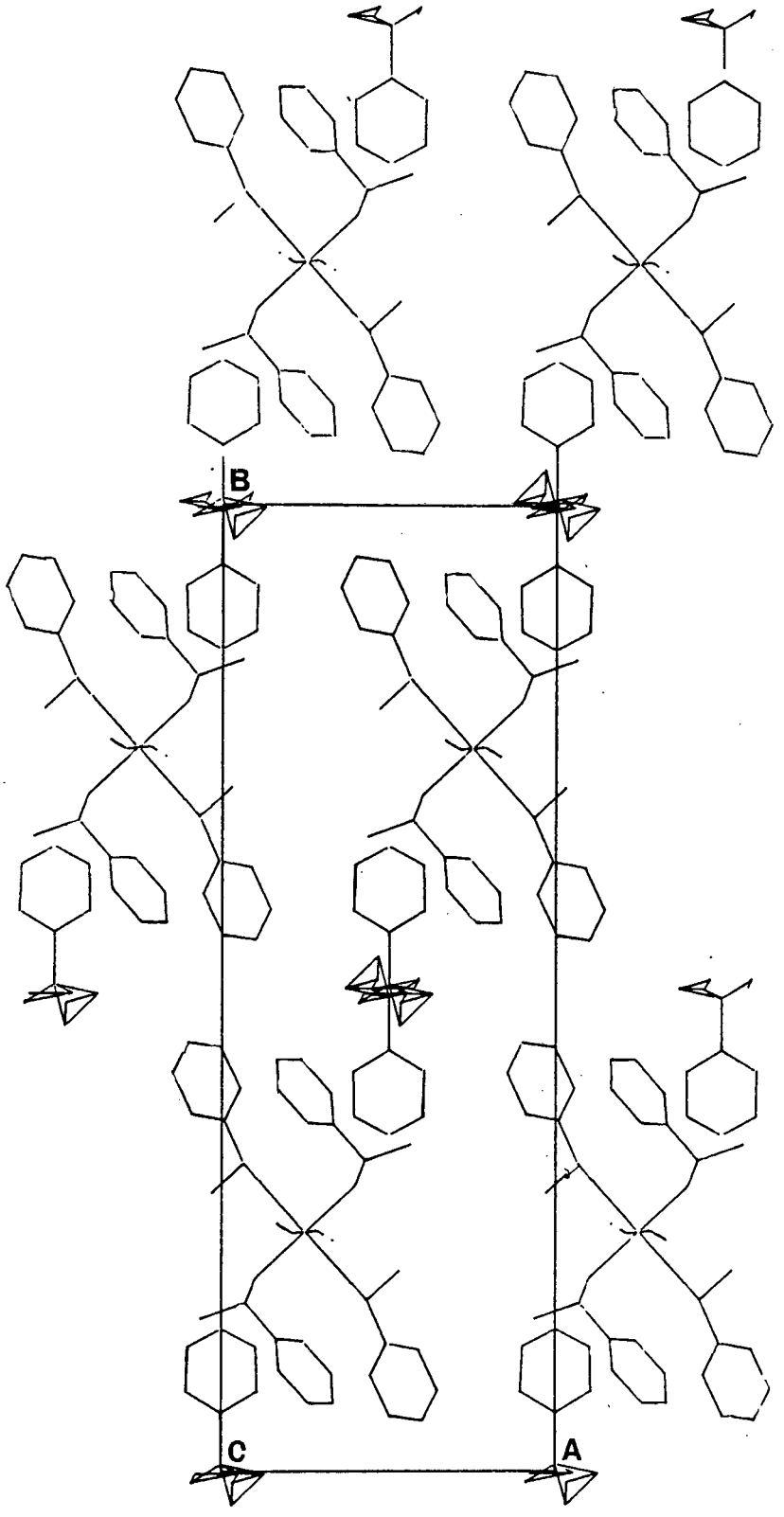


Figure 3.21 (b) Molecular packing viewed down the *z* axis.

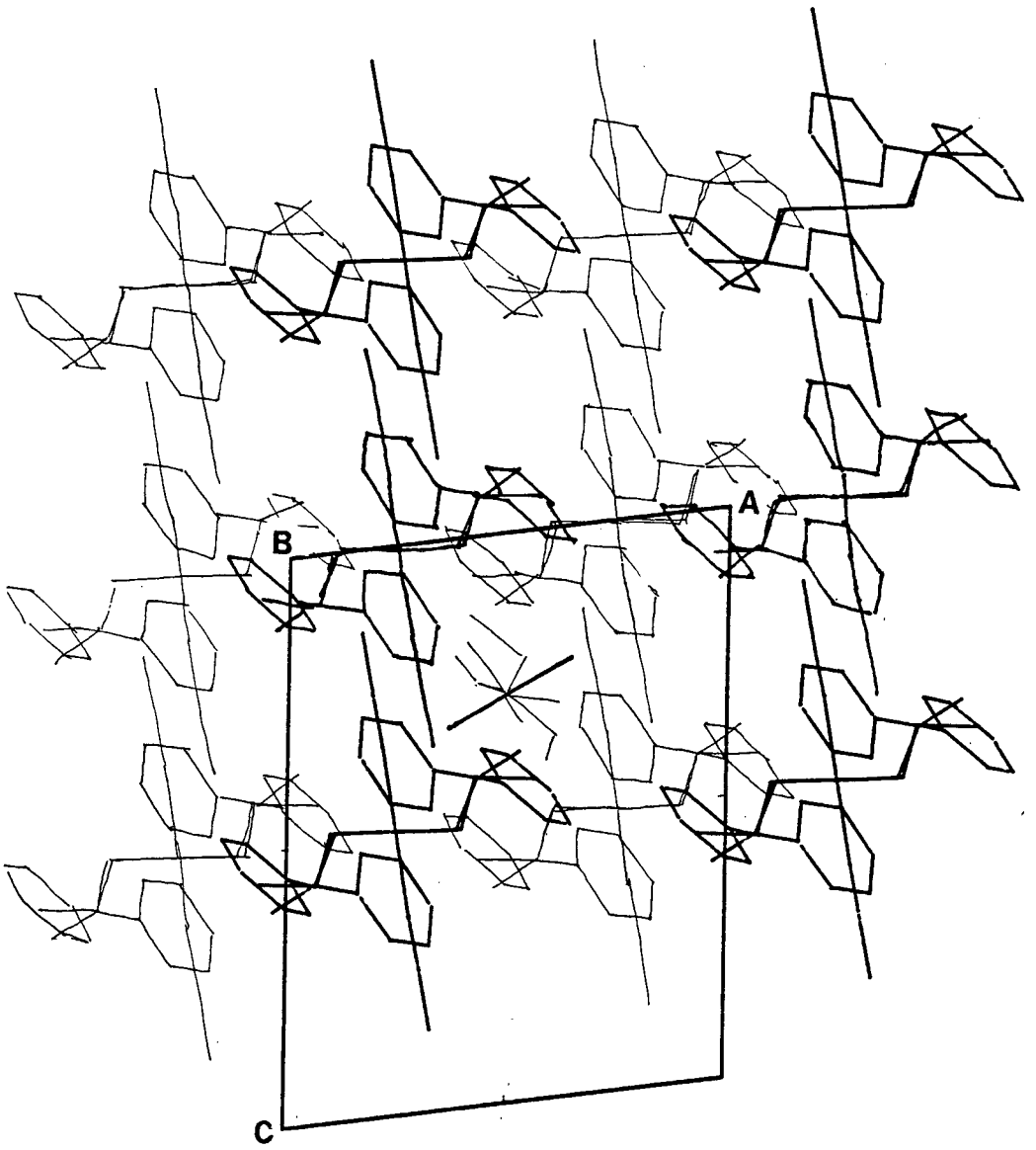


Figure 3.21 (c) Molecular packing viewed down the y axis.

TABLE 3.12 FRACTIONAL ATOMIC PARAMETERS AND THERMAL PARAMETERS ($U_{ij} \times 10^3$)

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
Ni	.2500	.2500	.5000	a
N1	.2182(8)	.2491(4)	.3489(6)	59(3)
C1	.1967(9)	.2528(5)	.2652(9)	52(3)
S1	.1670(3)	.2586(1)	.1458(2)	a
N2	.3996(9)	.2982(3)	.5092(8)	45(3)
C21	.4292(12)	.3246(5)	.4217(11)	60(5)
H211	.4202(12)	.3049(5)	.3629(11)	70(27)
C22	.5652(12)	.3410(5)	.4371(11)	88(5)
H221	.5914(12)	.3544(5)	.3766(11)	86(17)
H222	.6132(12)	.3133(5)	.4371(11)	86(17)
H223	.5831(12)	.3617(5)	.4937(11)	86(17)
C23	.3360(12)	.3619(4)	.3994(10)	54(4)
C24	.2578(12)	.3648(5)	.3121(10)	73(5)
H241	.2647(12)	.3422(5)	.2603(10)	88(5)
C25	.1685(15)	.3980(5)	.2924(12)	94(5)
H251	.1084(15)	.3986(5)	.2299(12)	113(6)
C26	.1674(14)	.4286(5)	.3607(12)	93(5)
H261	.1085(14)	.4537(5)	.3449(12)	111(6)
C27	.2387(14)	.4289(5)	.4494(11)	94(5)
H271	.2292(14)	.4522(5)	.4992(11)	112(7)
C28	.3268(13)	.3950(4)	.4692(11)	79(5)
H281	.3835(13)	.3945(4)	.5335(11)	95(6)
N3	.3868(9)	.1964(3)	.5105(8)	54(4)
C31	.4328(13)	.1787(4)	.4218(11)	60(5)
H311	.3558(13)	.1763(4)	.3720(11)	70(27)
C32	.5299(12)	.2093(4)	.3829(10)	70(4)
H321	.4825(12)	.2374(4)	.3728(10)	86(17)

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
H322	.5540(12)	.1987(4)	.3199(10)	86(17)
H323	.6076(12)	.2142(4)	.4319(10)	86(17)
C33	.4921(13)	.1334(4)	.4373(10)	67(4)
C34	.4457(15)	.1007(5)	.3726(12)	101(6)
H341	.3766(15)	.1062(5)	.3173(12)	122(7)
C35	.5037(17)	.0580(6)	.3895(13)	119(6)
H351	.4703(17)	.0325(6)	.3483(13)	143(8)
C36	.6010(16)	.0526(6)	.4599(12)	106(6)
H361	.6418(16)	.0232(6)	.4677(12)	127(7)
C37	.6476(16)	.0852(6)	.5217(13)	114(6)
H371	.7205(16)	.0799(6)	.5740(13)	137(7)
C38	.5903(14)	.1269(5)	.5100(11)	92(5)
H381	.6216(14)	.1515(5)	.5548(11)	111(6)
Atom (Guest)				
C10	.0000(0)	.1483(8)	.2500(0)	106(8)
C20	.1035(17)	.1292(6)	.2141(14)	131(7)
C30	.1062(18)	.0827(6)	.2155(15)	135(7)
C40	.0000	.0606(9)	.2500	114(9)
C50	.0000	.0064(14)	.2500	201(15)
C601	.0542(56)	-.0024(26)	.1640(42)	114(11)
C602	-.0749(67)	-.0025(45)	.1059(69)	114(11)
C603	.0324(77)	-.0358(18)	.3047(48)	114(11)
C611	.1280(47)	-.0032(29)	.3076(50)	114(11)
C612	.0358(68)	-.0124(44)	.3839(67)	114(11)
C613	-.0887(67)	-.0121(33)	.1619(52)	114(11)

a

Anisotropic thermal parameters ($U_{ij} \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	54(2)	42(1)	53(2)	0(2)	-4(1)	3(2)
S1	67(3)	87(3)	53(2)	9(3)	-3(2)	-5(3)

TABLE 3.13 BOND LENGTHS (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Host Molecule	
NI - N1	2.050(9)
NI - N2	2.170(10)
NI - N3	2.192(10)
N1 - C1	1.143(15)
C1 - S1	1.632(13)
N2 - C21	1.513(19)
C21 - C22	1.529(19)
C21 - C23	1.520(19)
C23 - C24	1.367(18)
C23 - C28	1.405(19)
C24 - C25	1.397(21)
C25 - C26	1.324(23)
C26 - C27	1.344(21)
C27 - C28	1.404(20)
N3 - C31	1.473(19)
C31 - C32	1.541(19)
C31 - C33	1.528(18)
C33 - C34	1.384(20)
C33 - C38	1.362(19)
C34 - C35	1.452(24)
C35 - C36	1.331(23)
C36 - C37	1.359(25)
C37 - C38	1.416(24)

Guest Molecule

C10 - C20	1.400(22)
C20 - C30	1.424(26)
C30 - C40	1.456(24)
C40 - C50	1.659(51)
C50 -- C601	1.407(63)
C601 - C602	1.500(92)
C50 - C603	1.510(68)
C50 - C611	1.516(54)
C611 - C612	1.557(112)
C50 - C613	1.539(74)
All C - H bond lengths[a]	1.00

[a]Bond lengths fixed

TABLE 3.14 BOND ANGLES (DEGREES) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Host Molecule				
N2	- NI	- N3	91.3	(.4)
N1	- NI	- N3	94.3	(.4)
N1	- NI	- N2	95.1	(.4)
NI	- N1	- C1	173.2	(1.2)
N1	- C1	- S1	179.3	(1.3)
NI	- N2	- C21	123.3	(.8)
N2	- C21	- C23	111.0	(1.1)
N2	- C21	- C22	111.3	(1.2)
C22	- C21	- C23	111.7	(1.2)
C21	- C23	- C28	120.6	(1.2)
C21	- C23	- C24	122.2	(1.2)
C24	- C23	- C28	117.2	(1.3)
C23	- C24	- C25	122.6	(1.3)
C24	- C25	- C26	116.7	(1.5)
C25	- C26	- C27	125.7	(1.5)
C26	- C27	- C28	117.1	(1.4)
C23	- C28	- C27	120.6	(1.3)
NI	- N3	- C31	121.1	(.8)
N3	- C31	- C33	133.5	(1.2)
N3	- C31	- C32	104.6	(1.5)
C32	- C31	- C33	108.1	(1.1)
C31	- C33	- C38	120.0	(1.2)
C31	- C33	- C34	117.4	(1.3)
C34	- C33	- C38	122.5	(1.3)
C33	- C34	- C35	-16.1	(1.5)

C34 - C35 - C36	120.3	(1.7)
C35 - C36 - C37	123.1	(1.7)
C36 - C37 - C38	118.3	(1.6)
C33 - C38 - C37	119.7	(1.4)

Guest Molecule

C10 - C20 - C30	115.3	(1.6)
C20 - C30 - C40	117.0	(1.5)
C30 - C40 - C50	117.7	(.8)
C40 - C50 - C601	101.0	(2.8)
C40 - C50 - C603	148.8	(2.5)
C40 - C50 - C611	101.2	(2.9)
C40 - C50 - C613	111.6	(3.0)
C50 - C601 - C602	89.4	(4.3)
C50 - C611 - C612	76.8	(3.9)
C601 - C50 - C603	99.1	(3.8)
C611 - C50 - C613	139.1	(4.4)

TABLE 3.15 SELECTED TORSION ANGLES

Host Molecule

Ni - N2 - C21 - C22	-156.62°	(.91)
Ni - N2 - C21 - C23	78.33°	(1.28)
N2 - C21 - C23 - C24	-117.64°	(1.42)
Ni - N3 - C31 - C32	76.05°	(1.24)
Ni - N3 - C31 - C33	-161.41°	(.87)
N3 - C31 - C33 - C34	125.99°	(1.38)

TABLE 3.16 WEIGHTED LEAST-SQUARES PLANES

Equations of least-squares planes are expressed as

M1xX + M2xY + M3xZ = D

PLANE 1: The benzene ring atoms C23, C24, C25, C26, C27, C28

M1 = .7432 (.0042)

M2 = .5398 (.0055)

M3 = -.3954 (.0056)

D = 5.9688 (.0767)

Sum $(D/S)^2$ for all atoms defining this plane = 3.401

Chi-squared at 95% for 3 degrees of freedom = 7.81

The group of atoms does not deviate significantly from planarity.

PLANE 2: The benzene ring atoms C33, C34, C35, C36, C37, C38

M1 = .7337 (.0051)

M2 = .2514 (.0064)

M3 = -.6313 (.0061)

D = .5666 (.0669)

Sum $(D/S)^2$ for all atoms defining this plane = 3.185

Chi-squared at 95% for 3 degrees of freedom = 3.84

The group of atoms does not deviate significantly from planarity.

PLANE 3: The benzene ring atoms of the guest molecule C10, C20, C30, C40

M1 = -.3733 (.0101)

M2 = -.0001 (.0016)

M3 = -.9277 (.0041)

D = -2.9735 (.0184)

Sum $(D/S)^2$ for all atoms defining this plane = .953

Chi-squared at 95% for 1 degree of freedom = 3.84

The group of atoms does not deviate significantly from planarity.

Dihedral angles formed by the least-squares planes:

Plane	- *Plane*	*Angle*	*(e.s.d.)*
1	2	21.48	(.48)
1	3	84.87	(.53)
2	3	71.84	(.63)

c) The Clathrate $[Ni(NCS)_2(\alpha\text{-Phenylethylamine})_4]$: n(*o*-Xylene)

Intensity data were obtained from a single crystal of the *o*-xylene clathrate. The dimensions of the orthorhombic unit cell found were:

$$a = 15.597(4)\text{Å}$$
$$b = 18.781(3)\text{Å}$$
$$c = 31.293(4)\text{Å}$$
$$\alpha = \beta = \gamma = 90^{\circ}$$

The cell volume of 9166.6Å^3 will accommodate eight host molecules; for the host structures reported earlier the molecular volume of the nickel complex is ≈880Å^3. Thus there remain ≈270Å^3 per host molecule, occupied by the guest compound. Allowing an estimated 19Å^3 for each non-hydrogen atom, the excess volume (corresponding to approximately 14 atoms by this estimation) indicates one (8 non-hydrogen atoms) or two (16 non-H atoms) guest molecules per host molecule.

E-statistics were typical of a centrosymmetric structure, and the systematic absences indicative of the space-group Pbcn (No.60).

The highest peaks in the Patterson map, corresponding to NixNi vectors, could be accounted for by a nickel atom in the general position (0.25, 0.11, 0.023). The isothiocyanate groups appeared in *trans*-positions, and when these and the remaining nitrogen atoms were placed around the nickel atom, the conventional residual was R=0.39. Difficulties experienced with the host structures described earlier were equally evident in subsequent structure solving.

Finally, when the four amine ligands (one of which appears disordered) and the phenyl-group of a guest molecule were also

included in the structure-factor calculation, a residual of R=0.26 was achieved. Further structure refinement, based on electron-density peaks in the SHELX Fourier map, three-dimensional electron-density contour maps and energy calculations, was unsuccessful. The Fourier maps depicting a complete molecule, clearly showing the disorder of one of the ligands and also the disordered guest molecule, are shown in Fig. 3.22. Fractional atomic parameters for the structure at this level of refinement are listed in Appendix 4.

Although the structure cannot be considered refined, the following observations are made:

1) The -NCS groups are in *trans*-positions, as in the *sec*-butylbenzene clathrate.

2) In the present structure model the nickel atoms have no site symmetry other than 1 (they fall on a general position), and no significant L.S. matrix correlation elements were found. Noting also that *o*-xylene is a more symmetrical molecule than *sec*-butylbenzene (the clathrate with the latter compound has the host molecule on an inversion center), the nickel complex in the present structure appears to be unsymmetrical.

3) As in the *sec*-butylbenzene clathrate, the phenyl groups of the amine ligands all point towards common planes: *yz*-planes (x/a = 0.0, 0.5) and *xy*-planes (z/c = 0.25, 0.75).

4) The nickel complexes are stacked in columns parallel to the *y* axis, the distance between alternate nickel atoms being 7.80Å.

5) In the best model obtained the guest molecules do not appear to be parallel to any phenyl groups of amine ligands, but are held between four such phenyl-groups of two consequ-

tive host molecules.

Packing diagrams for the best model obtained for the structure are shown in Fig. 3.23a (down the x axis) and Fig. 3.23b (down the z axis).

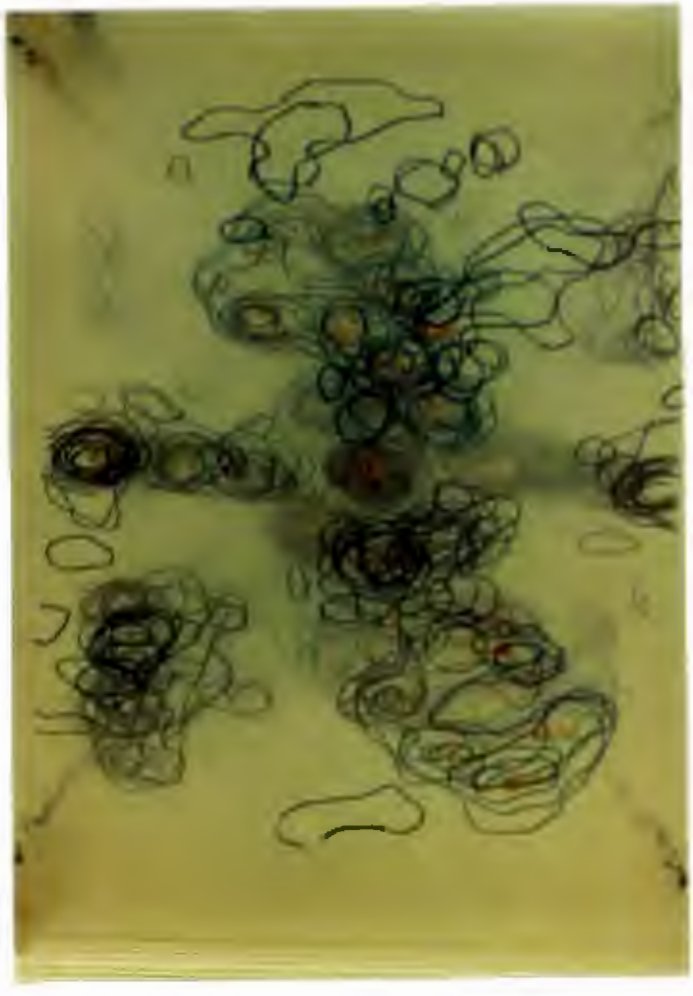
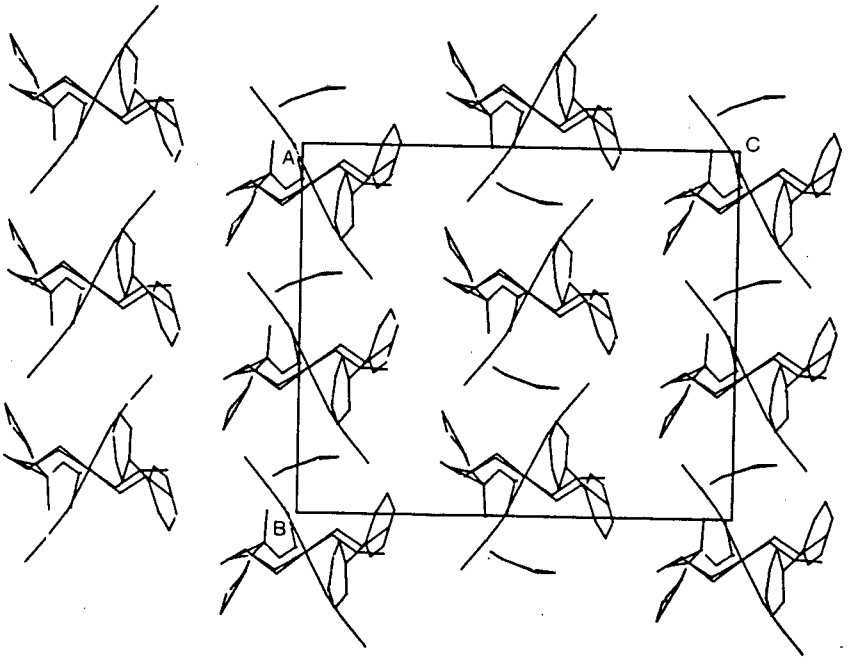
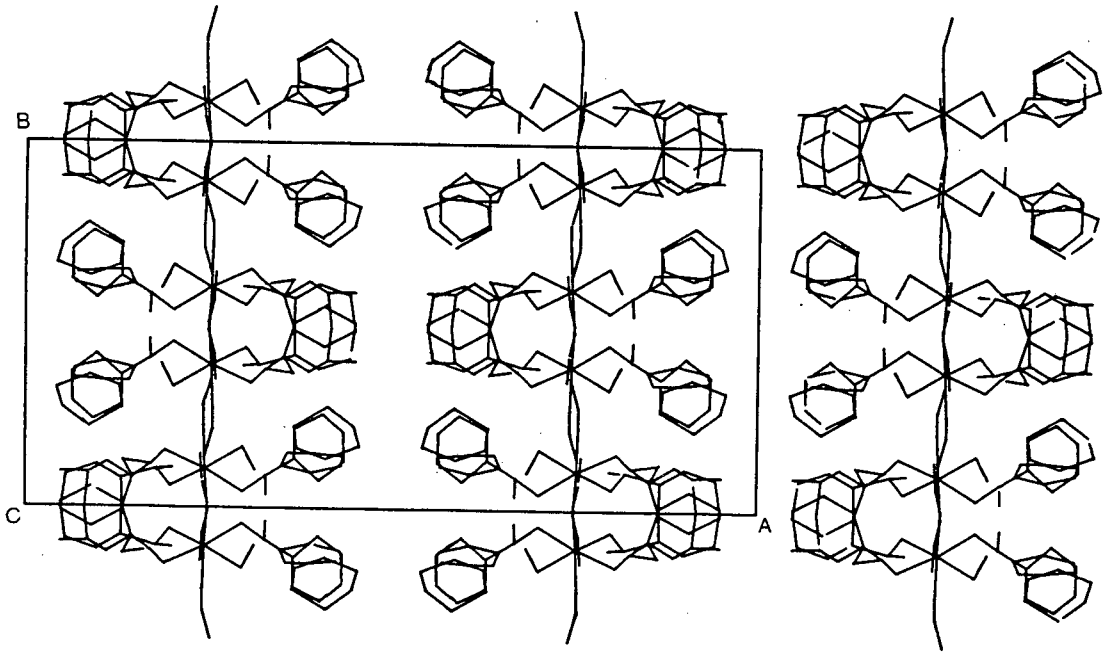


Figure 3.22 An electron density map showing one complete host molecule. The nickel atom appears in the centre, with -NCS groups on the left and right. The ligand visible in the upper part of the map has some significant electron density extending from the atom presently assigned -$\underline{C}H_3$.



(a) View down the x axis



(b) View down the z axis

Figure 3.23

3.1.3 An Energy Study of the Conformational Change of $[Ni(NCS)_2(\alpha\text{-Phenylethylamine})_4]$

The existence of the nickel complex in both *cis* and *trans* forms and the indication from the IR data of the occurrence of a conformational transformation of the solid complex as a Nujol mull, raised interest in the energy of conformational change. In a manner similar to the 'Berry pseudorotation' which models conformational change in triangular-bipyramidal complexes[86], the *trans*-to-*cis* transformation without bond-breaking of an octahedral complex may be modelled by rotating two opposite triangular faces of the octahedron with respect to each other. This is shown in Fig. 3.24.

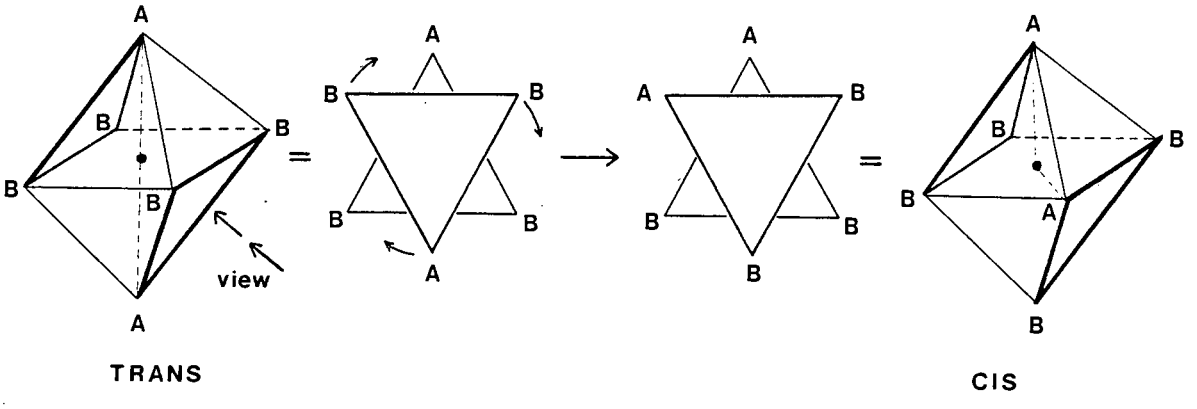


Figure 3.24 Conformational Transformation of an octahedral complex.

The intramolecular energy involved in a *trans-cis* transformation of the $[Ni(NCS)_2(\alpha\text{-phenylethylamine})_4]$ complex was modelled by calculating the non-bonded potential energies of one molecule as it was twisted to change conformation. The calculations were performed using the potential energy program EENY, which considers the non-bonded potential energies using empirical atom-pair curves of the form:

$$u(r) = a.\exp(-b.r)/r^d - c/r^6$$

Here r is the interatomic non-bonded distance between any pair of atoms and a, b, c and d are empirical constants given by Giglio[73]. The program only defines four types of atoms, C, H, N and Me. The $-CH_3$ groups of the amines, the sulphur and nickel atoms were therefore treated as Me-groups¶. Owing to these approximations only an estimate of the non-bonded intramolecular energies can be obtained.

The initial geometry of the nickel complex was taken from the crystal structure of its clathrate with *sec*-butylbenzene, i.e. the *trans*-isothiocyanate complex. In order to describe the rotation of the facing triangles of the octahedron, midpoints in two opposite N-N-N faces were found by simple vector averages in orthogonal space. Because dummy atoms in these N-N-N faces interfere with the calculations by forming close contacts with other atoms, two dummy atoms,D1 and D2, were defined on the vector-midpoints between the nickel atom and the midpoints of the N-N-N faces. (See Table 3.17.) The two dummy atoms were treated as hydrogen atoms.

A conformation-governing torsion angle, τ_o, was then defined as N11-D1-D2-N14, which in the crystal structure of the clathrate has a value of 179.9^o. This angle was then turned in steps of 10^o through 360^o. After every 10^o twist, 16 parameters (two angles and 14 torsion angles) were allowed to vary in

¶*As the nickel atom never forms non-bonded close contacts with other atoms, treating it as a ME group is not expected to significantly affect the calculations.*

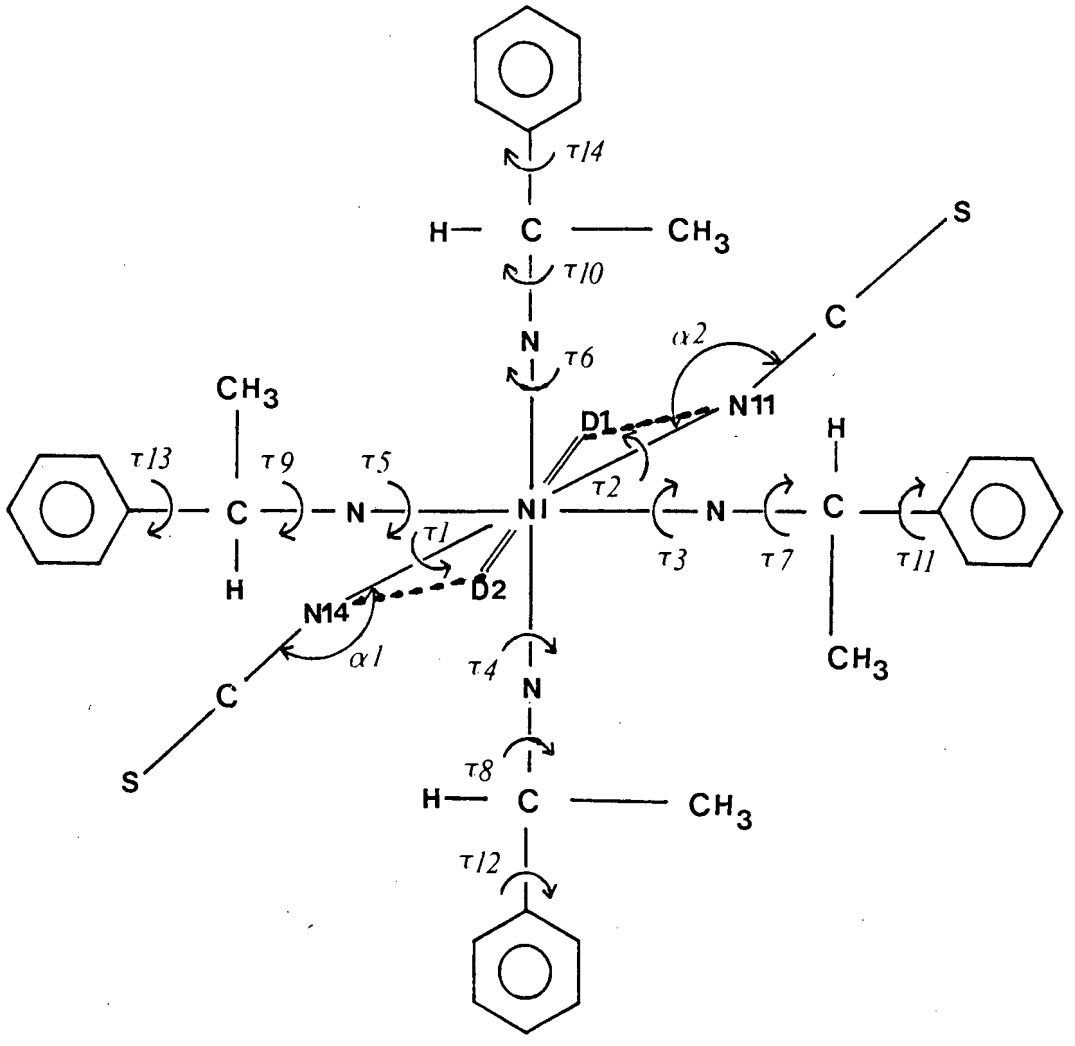
ATOM	ORTHOGONAL COORDINATES		
	X'	Y'	Z'
N11 (-CS)	1.6952	7.6235	4.7312
N12	3.3436	9.1261	6.9049
N13	3.2041	6.0106	6.9225
Midpoint	2.7465	7.5885	6.1862
NI	1.7575	7.6510	6.7802
D1	2.2520	7.6197	6.4832
N14 (-CS)	1.8197	7.6785	8.8291
N15	.1713	6.1759	6.6554
N16	.3109	9.2914	6.6378
Midpoint	.7669	7.7152	7.3741
NI	1.7575	7.6510	6.7802
D2	1.2662	7.6831	7.0772

Table 3.17 Derivation of dummy atom positions

order to achieve a minimum-energy structure. The variable parameters are shown in Fig.3.25.

The method used by the program EENY is to calculate an energy surface at a point by making small displacements in each parameter from that point. The parameters are then shifted 'downhill' an energy-gradient by a chosen step-size. If the energy at the new point is higher than the initial energy, a minimum 'valley' must have been crossed, and the step-size is halved. The iterative process is stopped when a shift of 0.125° in the angular parameters does not produce a lower energy.

Energy barriers to conformational change were expected when the two triangular faces are in eclipsed positions ($\tau_o = 0^{\circ}$, 120°, 240°), and energy minima when they are in staggered



Governing Torsion Angle τ_0 = N11 - D1 -D2 - N14

Figure 3.25 Schematic representation of the complex showing all variable parameters in the energy-minimization calculations.

positions (τ_o = 60°, 180°, 300°). The calculated intramolecular energy-sums in kcal/mol as a function of the dihedral angle τ_o are shown in Fig. 3.26.

The resulting energy-curve is not entirely symmetrical, which may be the result of a number of reasons:

1) The N-N-N faces are not exactly parallel, and when twisted by τ_o, some of the N-N distances of opposite faces in eclipsed positions become shorter than others. This distortion is not symmetrical - depending on whether τ_o is positive or negative, different distortions and ligand interactions will arise.

2) The relaxation of the variables may be insufficient before τ_o is changed by the next 10°.

3) The molecule may not be adequately described in terms of these variables.

It can be seen, however, that the calculated energy barrier for the *trans*-to-*cis* transformation through a 'gauche' conformation is 27-35kcal/mol, and for the *cis*-to-*cis* conformational change through an 'anti' eclipsed form it is ≃19kcal/mol. The energy difference between the *trans*- and *cis*-minima is 2 - 3kcal/mol, the *cis*-conformer being of the lower energy. Although little significance may be attached to such a small calculated energy difference, it points towards the fact that this nickel complex crystallizes in the *cis*-form rather than the *trans*-form, unless in the presence of some other compound with which it can co-crystallize.

The above calculated energy barriers may be compared to the following: 21kcal/mol for the (*M*)-(-)-TOT to (*P*)-(+)-TOT enantiomerization[35], which takes place rapidly at room temperature; 4.4 - 6.1kcal/mol for the rotation of butane through the eclipsed 'anti' form[26].

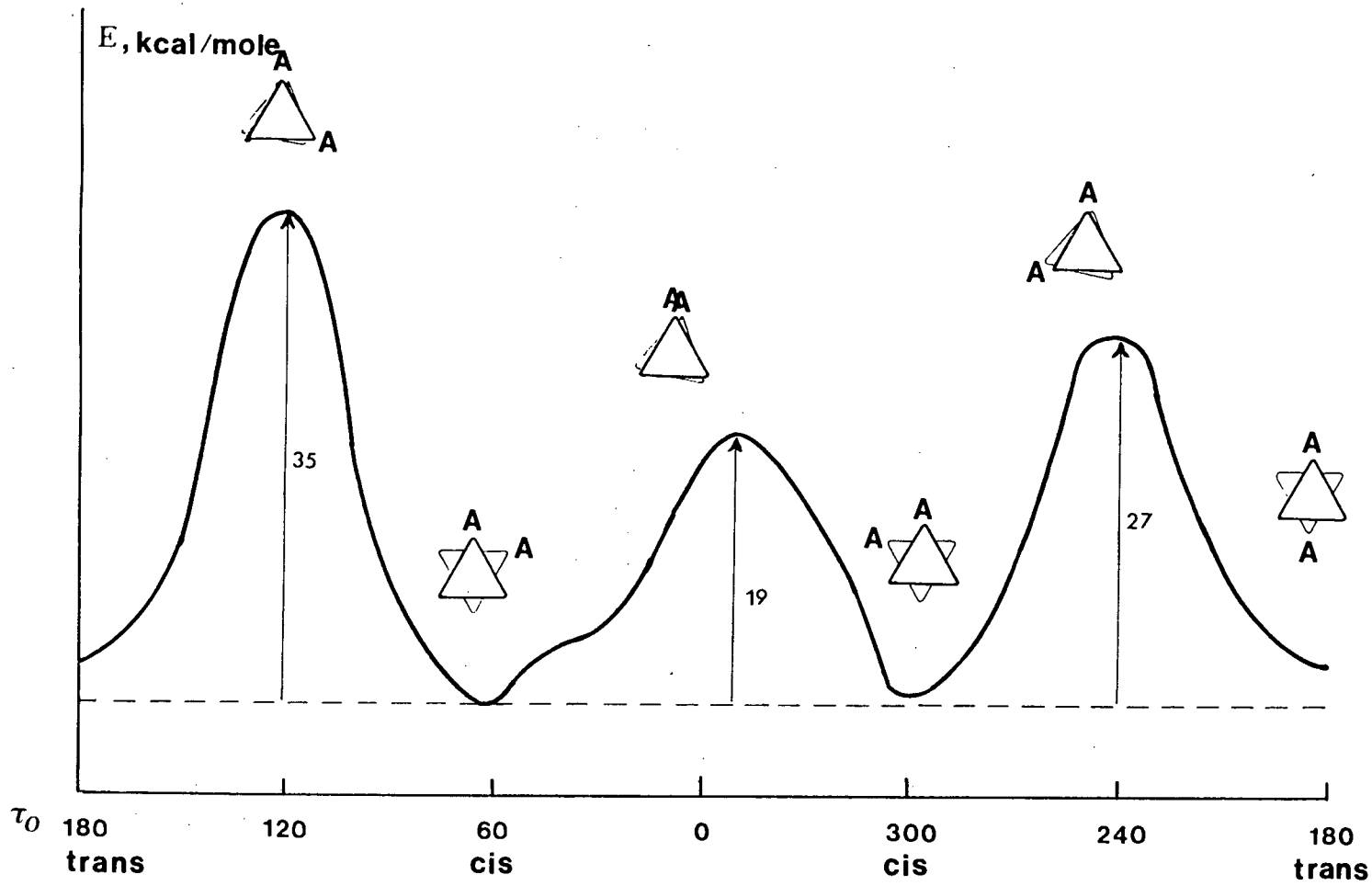


Figure 3.26 Calculated Potential Energy Curve for the *Trans*-to-*Cis* Transformation without Bond-Breaking of the Ni-complex

3.2 The Host Complexes and Attempted Clathrates of the Nickel Complex made with enantiomerically pure (*d*)- or (*l*)-α-Phenylethylamine

3.2.1 Initial characterization of the complexes

a) Microanalysis

The host complexes from enantiomerically pure amine both had similar percentage carbon, hydrogen and nitrogen content:

Found	61.7 %C	6.6 %H	12.7 %H
Calculated	61.3 %C	6.6 %H	12.7 %H

The values confirm the formation of the nickelbisisothiocyanate-tetramine complex.

The washed, unrecrystallized material obtained in an attempt to enaclathrate guest compounds with these host complexes was unsuitable for microanalysis owing to loss of weight. Single crystals obtained from a solution in methanol and some additional quantity of the guest compound, however, gave results similar to the above.

b) UV - Visible Spectroscopy

The spectra of the complexes made with the enantiomerically pure amine were identical to those obtained for the host complex made from a racemic mixture of the amine. Peaks were observed at $\lambda \simeq$ 310nm, 394nm and 644nm.

c) Mass Spectroscopy

The total ion current spectrum for crystals of the host

complex $[Ni(NCS)_2((\ell)$-α-phenylethylamine$)_4]$ is shown in Fig. 3.27a. Crystals of the attempted clathrate with *sec*-butylbenzene, recrystallized from methanol and a quantity of the guest compound, gave rise to the spectrum in Fig. 3.27b. The molecular radical spectrum (m/e = 134), corresponding to the 'guest' compound, is shown as a broken line curve in Fig. 3.27b. The presence of this peak indicated that the sample contained some *sec*-butylbenzene. This was first believed to possibly have been enclathrated, and some x-ray diffraction analyses were consequently performed on crystals of the attempted clathrate.

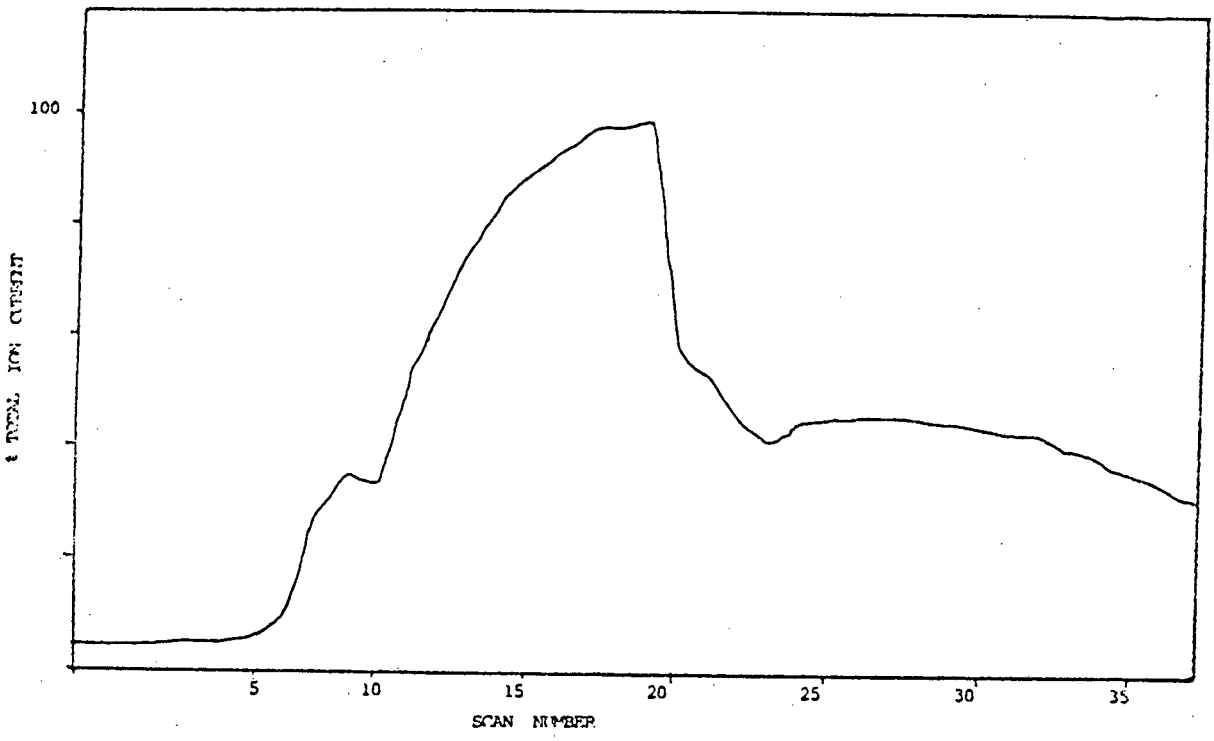
Fragmentation patterns were identical to those observed for the complexes made with the racemic amine (see Table 3.1).

d) Gas Chromatography

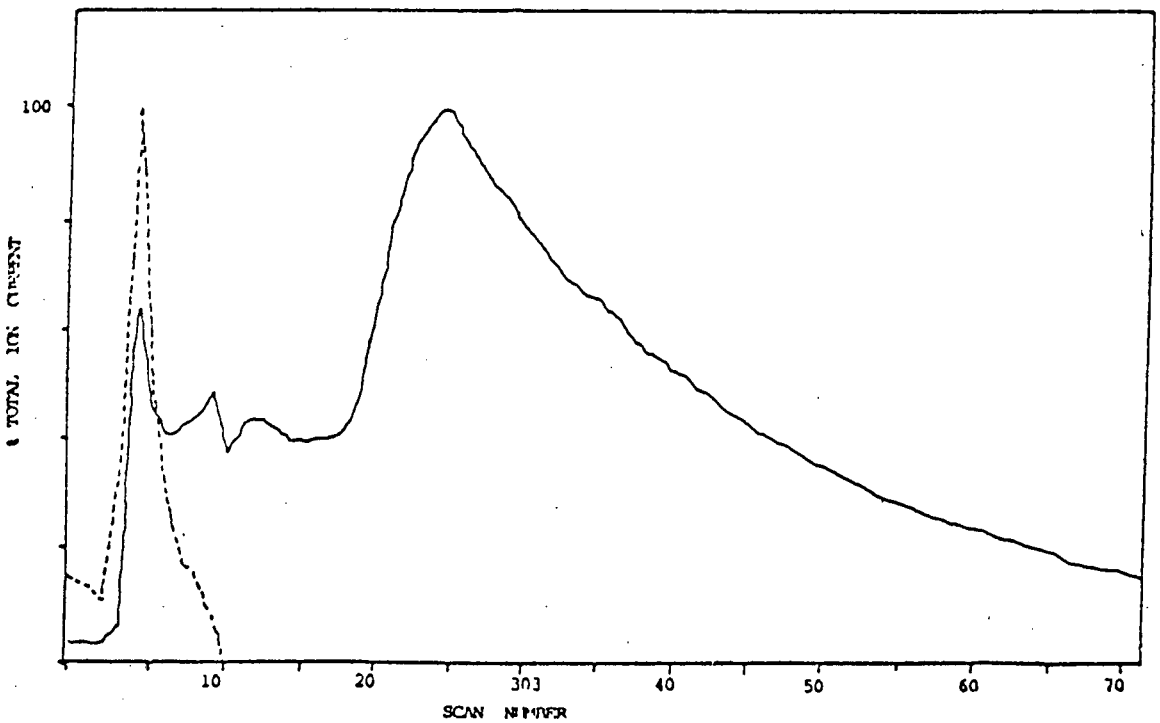
Column with (d)-ligand host

The net retention volumes of the aromatic compounds studied with the $(d\ell)$-host column were identical to those obtained for a column packed with 30% $Ni(NCS)_2((d)$-α-phenylethylamine$)_4$ on Chromosorb W. No separation of the *sec*-butylbenzene peak nor broadening of the peak was observed.

Although the surface of the (d)-ligand host necessarily has some chiral character, the interaction with the chiral *sec*-butylbenzene molecules is possibly such that the chiral parts of the latter are not directly involved in the surface interaction. This would explain the unaffected retention volume of the chiral substance.



(a) Total ion current spectrum of the (*l*)-ligand host complex



(b) Total ion current spectrum of the attempted clathrate between the (*l*)-ligand host and *sec*-butylbenzene

Figure 3.27

e) Nuclear Magnetic Resonance Spectroscopy

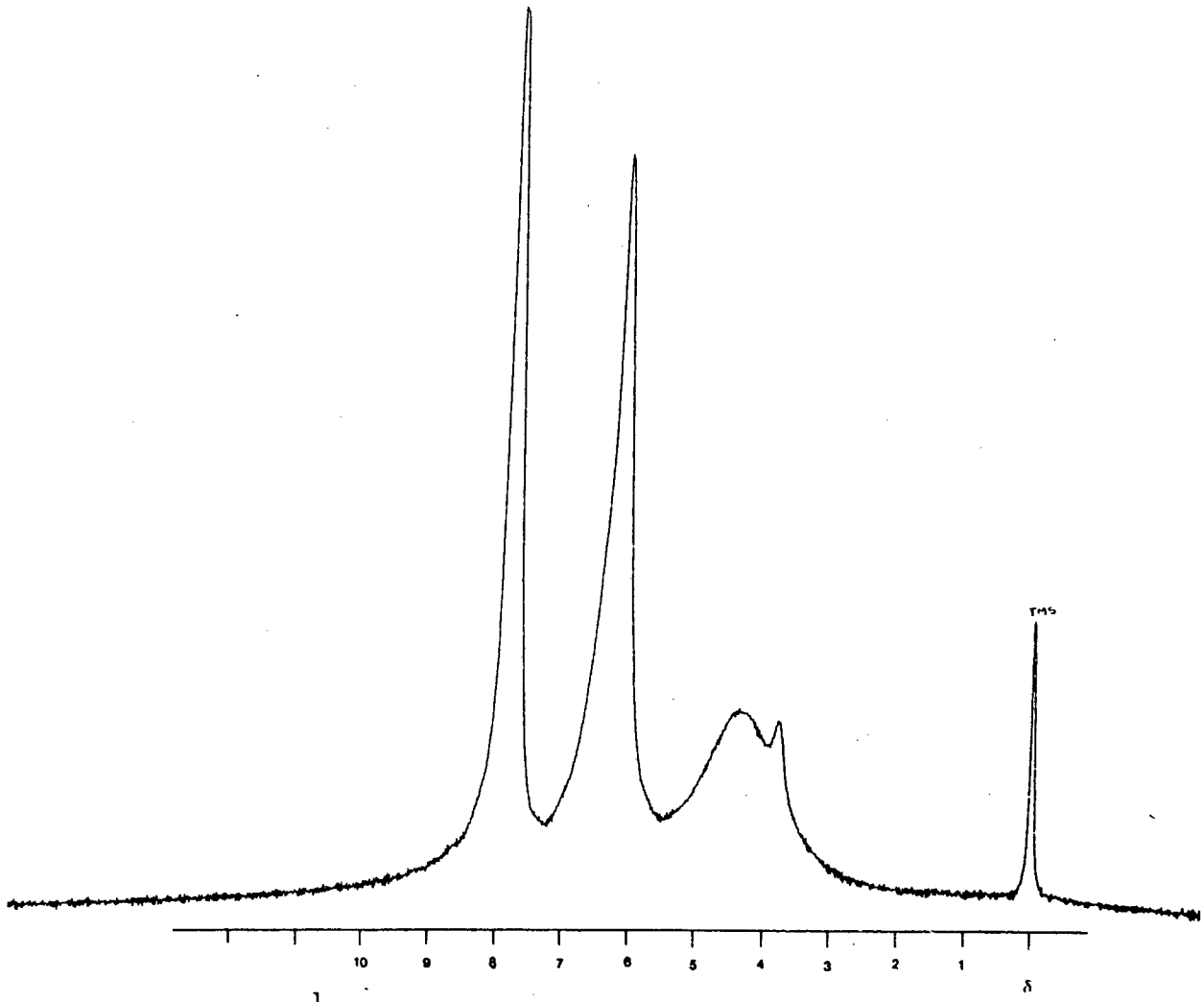
The room temperature spectra of the pure (*d*)-ligand host complex and the attempted clathrate with *sec*-butylbenzene were very similar to the spectra of the (*dl*)-ligand host complex and corresponding clathrate respectively. Consequently the variable temperature study was not repeated for these substances.

The only significant difference between the spectra of the host complexes is the appearance of the peak assigned to the ligand $-C\underline{H}_3$ methyl hydrogens. In the spectrum of the pure (*d*)-ligand host complex the peak is sharper than for the host complex with racemic amine, and it occurs at δ=4.1ppm (compared to δ=3.3ppm in the (*dl*)-ligand host complex). The spectrum of the (*d*)-ligand host complex appears in Fig. 3.28.

Considering the above observation and the extensive shift changes of the $-C\underline{H}_3$ peak when the host complex is cooled, it appears that the α-substituted methyl group is the part of the amine ligand most sensitive to conformational changes.

f) Infrared Spectroscopy

The IR spectra of the host complexes and attempted clathrates from enantiomerically pure amine ligands were identical to the spectrum of the (*dl*)-ligand host complex. This implies that an octahedral *cis*-isothiocyanate complex has been formed, similar to that of the (*dl*)-ligand host.



The ^{1}H NMR spectrum of the (*d*)-ligand host complex

Figure 3.28

g) X-Ray Powder Diffractometry

The x-ray diffractogram of the (*d*)-ligand complex was found to be superimposable on that obtained from the (*dl*)-ligand host compound.

The diffractogram of the (*d*)-ligand complex synthesized in the presence of *sec*-butylbenzene is shown in Fig.3.29. Some of the lines still coincide with those observed for the ordinary host complexes; however, the spectra are no longer superimposable.

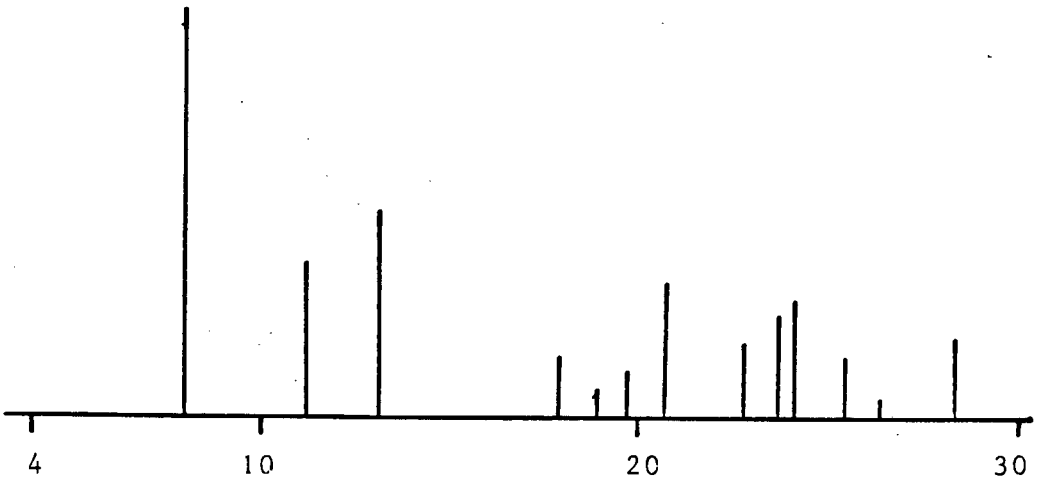


Figure 3.29 X-Ray Diffractogram of the (*d*)-ligand Complex Synthesized in the Presence of *Sec*-Butylbenzene

3.2.2 Single Crystal Structures

a) The Crystal and Molecular Structure of $[Ni(NCS)_2((R)\text{-}\alpha\text{-phenylethylamine})_4]$

i) Preliminary X-Ray Analysis

The oscillation, zero- and first-layer Weissenberg photographs from a single crystal of the nickel complex, which was made from pure (*d*)-α-phenylethylamine, had reflections in identical positions to those observed with the host complex from racemic amine (refer to Section 3.1.2a). The rules for non-extinction were also identical. Consequently the same unit cell and non-centrosymmetric space-group were derived for this structure:

$a = 15.5\text{Å}$ $\quad b = 15.3\text{Å}$ $\quad c = 14.7\text{Å}$

$\alpha = \beta = \gamma \simeq 90^{\circ}$

Space-Group $P2_12_12$ (No. 18)

ii) Intensity Data Collection

Accurate cell parameters were determined by least-squares analysis based on 25 reflections in the θ-range 12° - 14°. In order to achieve an unambiguous absolute configuration of the structure, Bijvoet pairs were collected (see also Appendix 1). The intensities of three standard reflections which were monitored during the data collection were stable to within 1.4% of their mean values.

The diffractometer data set contained 3821 unique reflections of which 2081 satisfied the criterion $I_{rel} > 2\sigma I_{rel}$, which were used in the structure solution and refinement. Accurate

cell dimensions and other relevant crystal data are listed in Table 3.18.

iii) Solution and Refinement of the Structure, Assignment of Absolute Configuration

The structure was solved by the heavy atom method. The Patterson peaks corresponding to the Ni×Ni vectors were almost identical to those observed for the host structure in Section 3.1.2a, attributable to nickel atoms on the special positions:

(0.0, 0.0, 0.421) and (0.0, 0.0, 0.921) (Wykhoff letter *a*)

The phasing problems which were encountered in solving the host structure described in section 3.1.2a were experienced once again: insertion of the isothiocyanate groups resulted in the appearance of six peaks at Ni-N distances around both nickel atoms (only three are expected), and even when most of the scattering matter was placed, the remaining atoms were not readily positioned.

The complete structure, including all hydrogen atoms in calculated positions and free $-N\underline{H}_2-$ hydrogens, but with no atoms treated anisotropically, was refined with f'' = 0.0 for all atom types. The residual obtained for this set of coordinates, $+x_j$, was $R_G = 0.0867$.

Two sets of structure factors, F_c, were then calculated without any further refinement, using the same isotropic thermal parameters and scale factor and +f'' for each dispersive atom: one for the coordinate set $+x_j$, and one for the inverse structure, $-x_j$. Two different residuals were

TABLE 3.18 CRYSTAL DATA

Molecular Formula	$C_{34}H_{44}N_6NiS_2$
Molecular Weight	$659.59 gmol^{-1}$
Space-Group	$P2_12_12$
a	15.587(3)Å
b	15.151(3)Å
c	14.773(2)Å
α	90.0°
β	90.0°
γ	90.0°
Volume	$3489(1)Å^3$
Z	4
D_c	$1.26 gcm^{-1}$
$\mu(MoK_\alpha)$	$6.56 mm^{-1}$
F(000)	1400
Crystal Dimensions	0.16 x 0.19 x 0.25mm
Scan mode	ω-2θ
Scan width	$(0.88+0.35\tan\theta)^\circ$
Vertical aperture length	4mm
Aperture width	(1.25+1.05tanθ)mm
Final acceptance limit	20σ at $20^\circ min^{-1}$ in ω
Maximum recording time	40s
Crystal stability	1.4%
Range scanned	$1 - 20^\circ\theta$
Total number of reflections	3821
Final Refinement Data	
R	0.078
R_w	0.065
S	2.85
N	2081
NP	198

obtained:

$$R_G^+ = 0.0881 \qquad \text{and} \qquad R_G^- = 0.0909$$

Using Hamilton's test[85], the hypothesis that the structure with the higher residual was the better model of the measured intensities could be rejected at a significance level of 0.005. The absolute structure therefore corresponds to the coordinate set $+x_j$, in which the structure was initially solved. The absolute configuration of the amine ligand can now be derived from the structure.

The (*d*)-α-phenylethylamine ligand has an α-carbon atom with the absolute configuration (*R*).

When the structure with the lower residual was refined to shift < $^1/_{50}$esd for all parameters, nickel and sulphur atoms treated anisotropically and a weighting scheme $w = 1/\sigma^2 F$, the final residual obtained was R = 0.0779 (R_w = .0654), corresponding to a goodness-of-fit parameter S = 2.85.

Positional atomic parameters and temperature factors are listed in Table 3.25. Observed and calculated structure factors appear in Appendix 7.

iv) Description of the Structure

1) Molecular Structure

Perspective views of the two independent molecules, showing atomic nomenclature, appear in Fig. 3.30. Molecular bond distances and bond angles are listed in Tables 3.20 and 3.21 respectively. Selected torsion angles appear in Table 3.22 and weighted least squares planes of the phenyl groups in Table 3.23.

Molecule 1

This molecule resembles almost exactly the 'Molecule 1' in the crystal structure containing one molecule with four (*R*)-α-C amines and one molecule with two amines each of either chirality. The molecules may be compared by the conformation governing torsion angles listed in Tables 3.9 and 3.22. In both structures the molecule has four (*R*)-α-phenylethylamine ligands. For a description of the molecular structure, see Section 3.1.2a(iv).

Molecule 2

This molecule is chemically exactly the same as Molecule 1, but differs in conformation. The Ni-N-CS angles are considerably less linear (142.5° *vs.* 173.6° in Molecule 1). The conformation of the amines *trans* to the isothiocyanates is preserved, which is evident from the torsion angles in Table 3.22. The remaining two amines, however, have a considerably altered conformation, which is primarily the result of rotation about the N23-C231 bond. In essence, going from Molecule 1 to Molecule 2 the position of the methyl group (corresponding to C132) has been exchanged for that of the phenyl group by a suitable rotation, with consequent exchange of methyl and hydrogen substituents of the α-C atom.

An even more rewarding comparison, however, is that between Molecule 2 of this structure and Molecule 2 of the host structure described earlier. That complex has two amine ligands with an (*R*)-configuration and two with the (*S*)-configuration, while here all the amines are in the (*R*)-form. In both molecules the isothiocyanates and (*R*)-amines

trans to them have very similar conformations in both molecules. The conformation of the (*R*)-amines of Molecule 2 in the present structure, however, is such that the positions of the phenyl and methyl groups are retained as closely as possible (compared to the (*S*)-ligands in Molecule 2 of the host structure described earlier). This is achieved by a shift in the position of the α-carbon atom from one side of the N13-C132-C133 plane to the other side. The atom displaced furthest in this 'flip' is the hydrogen substituent (H631).

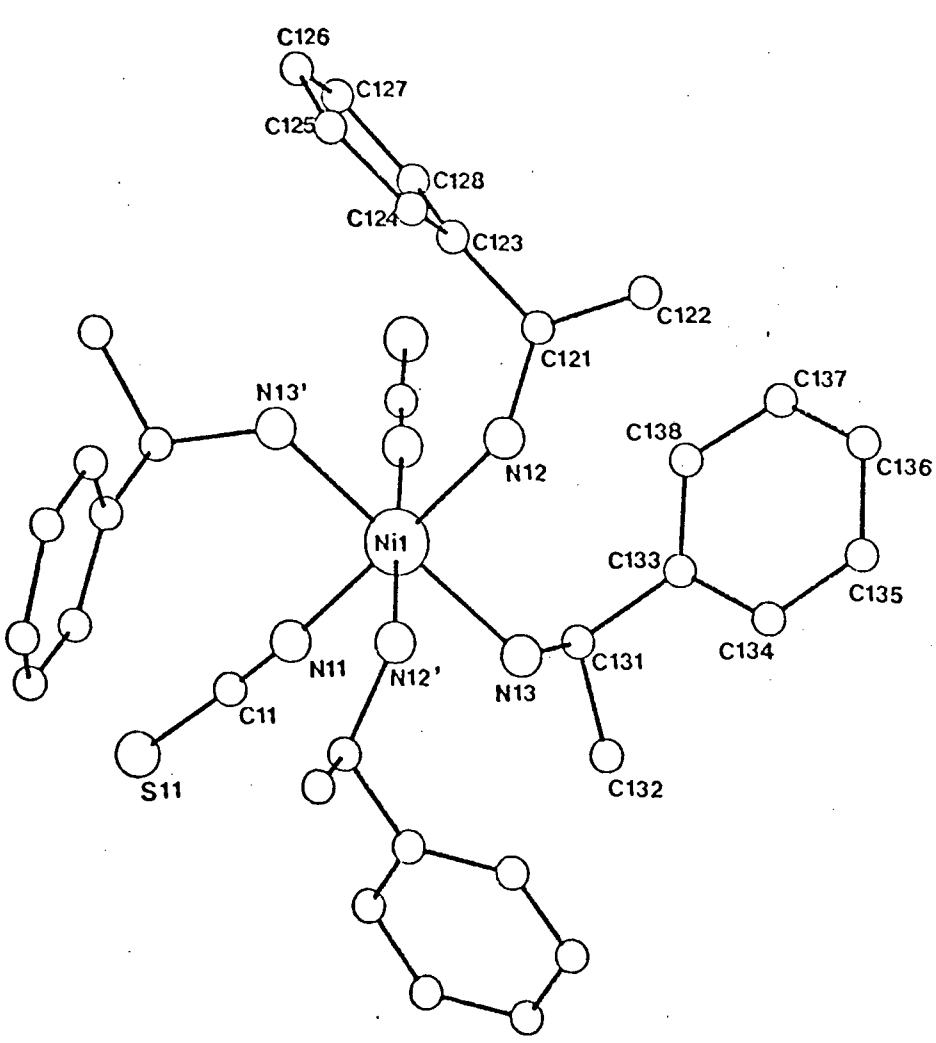
2) Molecular Packing

The packing of the tetramine molecules is illustrated in projections along the (010) and (001) directions in Fig.3.31.

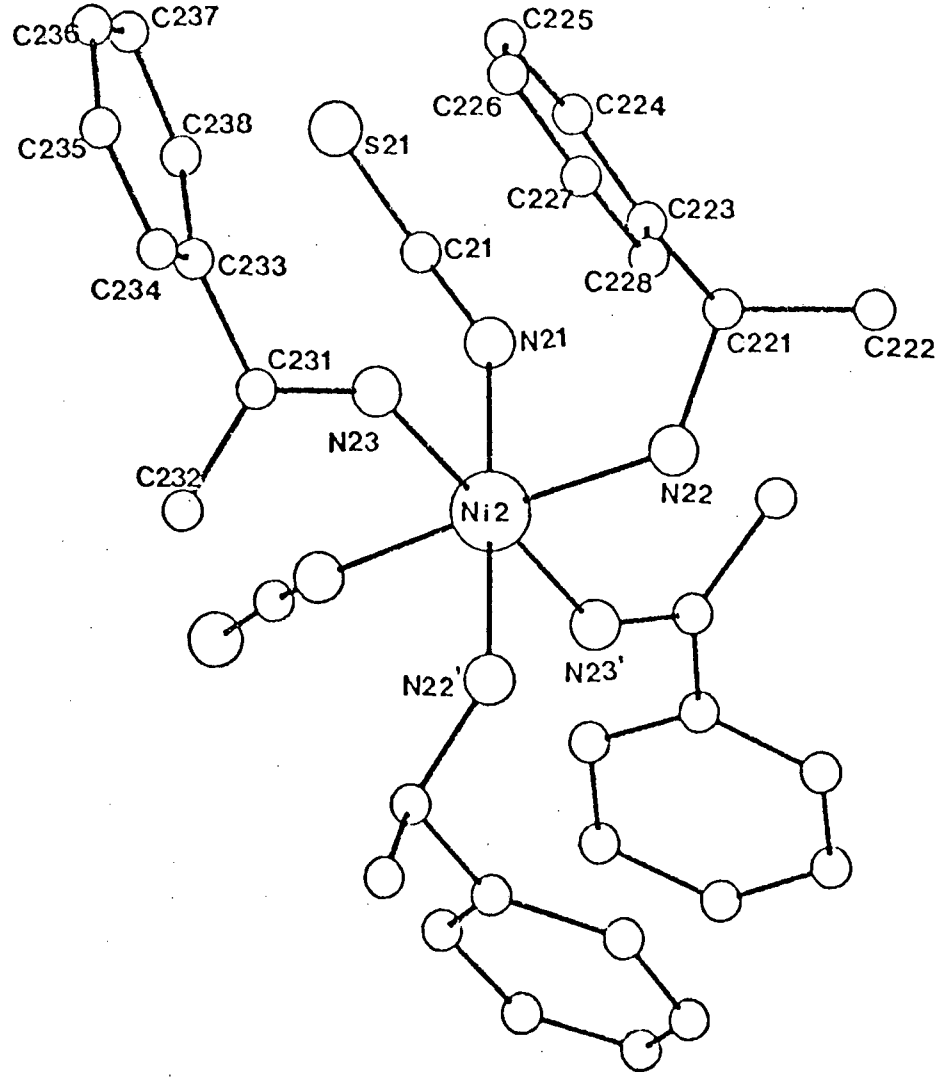
The structure consists of discrete, acentric molecules of the two types described above. The molecular packing is identical to the packing in the host structure described earlier, and a description is found in Section 3.1.2a(iv).

It is important to note that a conformational difference between two chemically equivalent molecules in this structure allows them to pack in the same manner as two chemically different molecules as in the host structure described earlier. The fact that not all molecules in this structure adopt the same conformation, and that no crystal was found which only had molecules containing two (*R*)- and two (*S*)-ligands (made from the racemic mixture), are indications that intermolecular interactions during crystallization play an important rôle in these substances. There are, however,

no obvious indications in the crystal structure as to the nature of any such interactions.

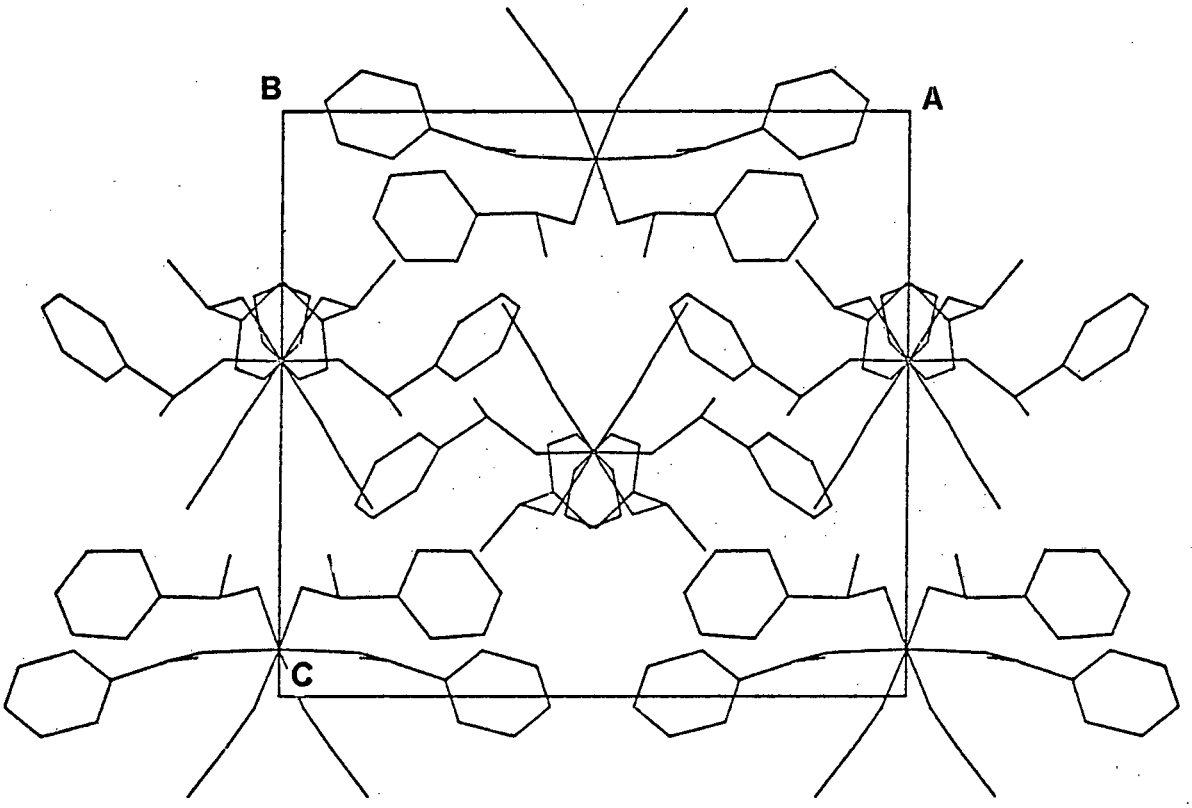


(a) Molecule 1



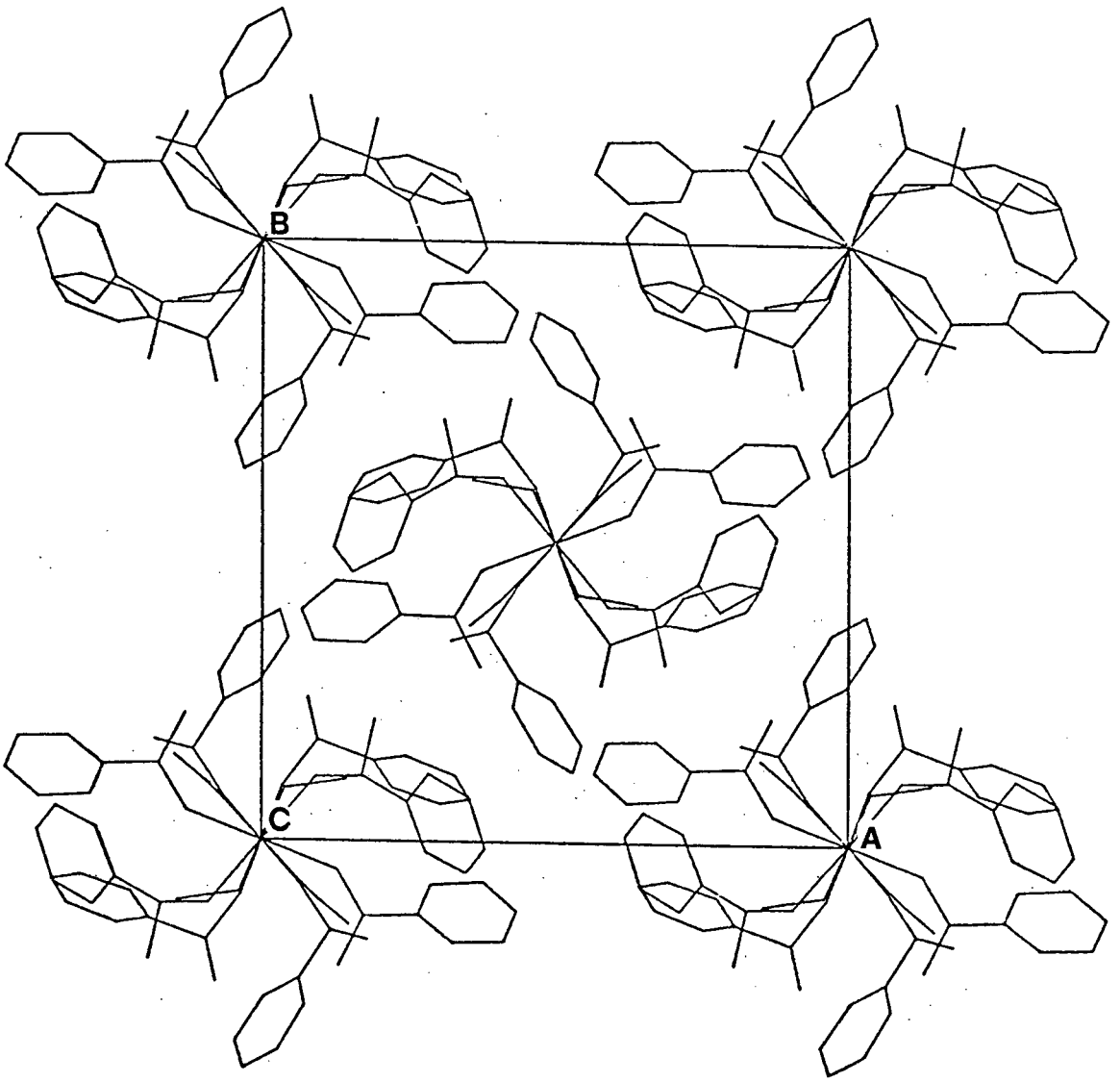
(b) Molecule 2

Figure 3.30



(a) Molecular packing : View down the y axis

Figure 3.31



(b) Molecular packing : View down the *z* axis

Figure 3.31

TABLE 3.19 FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS ($Uij \times 10^3$)

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
Molecule 1				
Ni1	.5000	.5000	.5766(3)	a
N11	.4366(9)	.4328(10)	.4749(10)	43(5)
C11	.4034(11)	.4018(12)	.4130(14)	35(6)
S11	.3525(4)	.3603(4)	.3268(5)	a
N12	.5639(11)	.5697(11)	.6836(12)	35(5)
H121	.5154(60)	.5941(70)	.7052(60)	30(46)
H122	.6077(76)	.5256(102)	.6789(111)	222(108)
C121	.6175(11)	.6499(11)	.6646(13)	31(5)
H621	.6522(11)	.6386(11)	.6089(13)	329(90)
C122	.6791(13)	.6647(14)	.7461(14)	72(7)
H622	.7081(13)	.7181(14)	.7206(14)	58(17)
H623	.7231(13)	.6185(14)	.7596(14)	58(17)
H624	.6484(13)	.6811(14)	.8031(14)	58(17)
C123	.5643(12)	.7311(12)	.6452(12)	42(6)
C124	.5046(14)	.7632(11)	.7072(11)	45(5)
H124	.4973(14)	.7335(11)	.7672(11)	146(20)
C125	.4554(12)	.8374(13)	.6867(14)	61(7)
H125	.4094(12)	.8579(13)	.7289(14)	146(20)
C126	.4695(12)	.8817(14)	.6070(14)	64(7)
H126	.4368(12)	.9371(14)	.5941(14)	146(20)
C127	.5274(11)	.8518(13)	.5458(14)	56(7)
H127	.5373(11)	.8845(13)	.4879(14)	146(20)
C128	.5732(11)	.7748(12)	.5647(13)	48(6)
H128	.6135(11)	.7512(12)	.5180(13)	146(20)

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
N13	.5914(11)	.3939(11)	.5784(14)	48(5)
H131	.5499(63)	.3567(55)	.5396(76)	41(48)
H132	.6052(81)	.4058(83)	.6321(71)	95(78)
C131	.6698(11)	.3928(12)	.5169(12)	28(5)
H631	.6577(11)	.4275(12)	.4608(12)	329(90)
C132	.6913(12)	.2991(11)	.4868(12)	57(7)
H632	.7347(12)	.2940(11)	.4372(12)	58(17)
H633	.6337(12)	.2811(11)	.4635(12)	58(17)
H634	.7081(12)	.2598(11)	.5382(12)	58(17)
C133	.7466(11)	.4341(12)	.5702(13)	40(5)
C134	.7836(12)	.3886(13)	.6417(12)	57(7)
H134	.7612(12)	.3290(13)	.6588(12)	146(20)
C135	.8522(15)	.4260(14)	.6915(15)	79(8)
H135	.8807(15)	.3925(14)	.7415(15)	146(20)
C136	.8800(11)	.5115(14)	.6670(14)	72(6)
H136	.9238(11)	.5422(14)	.7051(14)	146(20)
C137	.8466(13)	.5523(14)	.5931(15)	69(7)
H137	.8722(13)	.6094(14)	.5727(15)	146(20)
C138	.7782(11)	.5166(12)	.5442(11)	49(6)
H138	.7526(11)	.5499(12)	.4923(11)	146(20)
Molecule 2				
Ni2	.5000	.5000	.0816(3)	a
N21	.5394(10)	.4121(12)	-.0210(11)	59(6)
C21	.5819(13)	.4077(14)	-.0886(16)	49(7)
S21	.6432(4)	.3966(4)	-.1746(4)	a
N22	.5344(12)	.4088(13)	.1 89(13)	52(6)
H221	.4658(56)	.4039(68)	.2048(71)	106(47)
H222	.5732(65)	.4548(53)	.2183(55)	120(40)
C221	.5949(13)	.3322(13)	.1710(14)	58(7)
H721	.6486(13)	.3170(13)	.1373(14)	329(90)

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
C222	.5781(13)	.2626(13)	.2449(14)	75(7)
H722	.6207(13)	.2159(13)	.2286(14)	57(17)
H723	.5188(13)	.2377(13)	.2414(14)	57(17)
H724	.5895(13)	.2837(13)	.3079(14)	57(17)
C223	.6891(11)	.3668(11)	.1745(15)	43(5)
C224	.7426(14)	.3574(12)	.1009(14)	69(7)
H224	.7223(14)	.3284(12)	.0440(14)	146(20)
C225	.8281(15)	.3903(14)	.1084(15)	75(8)
H225	.8686(15)	.3824(14)	.0565(15)	146(20)
C226	.8538(14)	.4311(13)	.1823(16)	69(8)
H226	.9128(14)	.4570(13)	.1838(16)	146(20)
C227	.8049(16)	.4478(15)	.2535(17)	94(9)
H227	.8292(16)	.4647(15)	.3097(17)	146(20)
C228	.7207(12)	.4107(13)	.2542(14)	57(6)
H228	.6831(12)	.4199(13)	.3082(14)	146(20)
N23	.6279(13)	.5492(15)	.0796(16)	93(7)
H231	.6208(55)	.5522(79)	.0080(56)	217(35)
H232	.6450(55)	.4852(62)	.0551(98)	42(54)
C231	.6702(20)	.6229(20)	.0605(21)	131(12)
H731	.7286(20)	.6456(20)	.0762(21)	329(90)
C232	.6285(15)	.7077(13)	.0655(15)	93(8)
H732	.6601(15)	.7415(13)	.1131(15)	58(17)
H733	.5658(15)	.7080(13)	.0795(15)	58(17)
H734	.6383(15)	.7359(13)	.0051(15)	58(17)
C233	.7648(14)	.6218(13)	.0273(15)	60(7)
C234	.8256(14)	.6693(13)	.0787(16)	74(7)
H234	.8079(14)	.7043(13)	.1330(16)	146(20)
C235	.9107(14)	.6655(14)	.0517(14)	73(7)
H235	.9552(14)	.7011(14)	.0840(14)	146(20)
C236	.9342(14)	.6160(14)	-.0181(14)	72(8)

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
H236	.9964(14)	.612 (14)	-.0340(14)	146(20)
C237	.8770(13)	.5671(13)	-.0691(15)	70(7)
H237	.8965(13)	.5305(13)	-.1216(15)	146(20)
C238	.7877(12)	.5731(13)	-.0457(14)	61(7)
H238	.7431(12)	.5407(13)	-.0813(14)	146(20)

---

a

Anisotropic thermal parameters ($U_{ij} \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni1	37(3)	37(3)	36(3)	0	0	-2(3)
S11	87(5)	84(5)	45(5)	-5(5)	-16(5)	-32(5)
Ni2	40(3)	55(4)	43(4)	0	0	15(3)
S21	73(5)	64(4)	37(4)	-9(4)	-7(4)	6(4)

TABLE 3.20 BOND DISTANCES (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Molecule 1			*Molecule 2*		
Ni1 - N11		2.067(15)	Ni2 - N21		2.109(17)
Ni1 - N12		2.146(18)	Ni2 - N22		2.170(20)
Ni1 - N13		2.148(17)	Ni2 - N23		2.129(21)
N11 - C11		1.151(25)	N21 - C21		1.200(28)
C11 - S11		1.627(21)	C21 - S21		1.599(23)
N12 - C121		1.501(24)	N22 - C221		1.519(29)
C121 - C122		1.556(28)	C221 - C222		1.540(29)
C121 - C123		1.511(25)	C221 - C223		1.560(23)
C123 - C124		1.393(26)	C223 - C224		1.378(29)
C124 - C125		1.394(27)	C224 - C225		1.427(32)
C125 - C126		1.373(29)	C225 - C226		1.317(32)
C126 - C127		1.355(28)	C226 - C227		1.303(34)
C127 - C128		1.396(26)	C227 - C228		1.375(31)
C128 - C123		1.368(26)	C228 - C223		1.439(29)
N13 - C131		1.523(25)	N23 - C231		1.327(38)
C131 - C132		1.525(25)	C231 - C232		1.442(37)
C131 - C133		1.564(25)	C231 - C233		1.554(38)
C133 - C134		1.387(26)	C233 - C234		1.412(31)
C134 - C135		1.416(29)	C234 - C235		1.386(31)
C135 - C136		1.413(30)	C235 - C236		1.327(30)
C136 - C137		1.358(30)	C236 - C237		1.383(30)
C137 - C138		1.397(27)	C237 - C238		1.437(28)
C138 - C133		1.397(26)	C238 - C233		1.355(30)
All C - H bond lengths[a]			1.00 Å		

[a]Bond lengths fixed

TABLE 3.21 BOND ANGLES (DEGREES) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Molecule 1	
N11 - Ni1 - N13	87.6(.6)
N12 - Ni1 - N13	92.9(.7)
N11 - Ni1 - N12	179.0(.6)
N11 - C11 - S11	177.4(1.7)
Ni1 - N11 - C11	173.6(1.5)
Ni1 - N12 - C121	121.3(1.2)
N12 - C121 - C122	108.4(1.5)
N12 - C121 - C123	112.9(1.5)
C122 - C121 - C123	111.6(1.5)
C121 - C123 - C124	121.7(1.6)
C121 - C123 - C128	120.2(1.7)
C124 - C123 - C128	118.0(1.7)
C123 - C124 - C125	120.4(1.7)
C124 - C125 - C126	119.5(1.8)
C125 - C126 - C127	121.0(1.9)
C126 - C127 - C128	119.1(1.8)
C127 - C128 - C123	121.8(1.8)
Ni1 - N13 - C131	122.2(1.2)
N13 - C131 - C132	111.1(1.4)
N13 - C131 - C133	108.0(1.5)
C132 - C131 - C133	110.6(1.4)
C131 - C133 - C134	120.2(1.6)
C131 - C133 - C138	119.3(1.6)
C134 - C133 - C138	120.5(1.7)
C133 - C134 - C135	120.7(1.8)
C134 - C135 - C136	117.7(1.9)
C135 - C136 - C137	120.4(1.9)

C136 - C137 - C138	122.1(1.9)
C137 - C138 - C133	118.3(1.7)
Molecule 2	
N22 - Ni2 - N23	90.1(.8)
N21 - Ni2 - N22	92.9(.7)
N21 - Ni2 - N23	86.5(.7)
N21 - C21 - S21	175.6(2.0)
Ni2 - N21 - C21	142.5(1.6)
Ni2 - N22 - C221	120.9(1.3)
N22 - C221 - C222	107.1(1.6)
N22 - C221 - C223	107.4(1.6)
C222 - C221 - C223	109.9(1.6)
C221 - C223 - C224	117.0(1.8)
C221 - C223 - C228	123.0(1.8)
C224 - C223 - C228	119.1(1.7)
C223 - C224 - C225	117.9(1.8)
C224 - C225 - C226	120.8(2.1)
C225 - C226 - C227	121.9(2.2)
C226 - C227 - C228	122.8(2.3)
C227 - C228 - C223	117.3(1.9)
Ni2 - N23 - C231	139.7(1.9)
N23 - C231 - C232	121.0(2.6)
N23 - C231 - C233	122.0(2.4)
C232 - C231 - C233	117.0(2.3)
C231 - C233 - C234	117.5(2.0)
C231 - C233 - C238	120.5(2.0)
C234 - C233 - C238	121.9(2.0)
C233 - C234 - C235	117.8(2.0)
C234 - C235 - C236	120.8(2.1)
C235 - C236 - C237	123.3(2.0)

C237 - C237 - C238	117.4(1.9)
C237 - C238 - C233	118.8(1.9)

TABLE 3.22 SELECTED TORSION ANGLES

Molecule 1	*Angle (Degrees)*
Ni1 - N12 - C121 - C122	-160.2(1.2)
Ni1 - N12 - C121 - C123	75.6(1.8)
N12 - C121 - C123 - C128	-121.4(1.9)
Ni1 - N13 - C131 - C132	-145.0(1.4)
Ni1 - N13 - C131 - C133	93.5(1.6)
N13 - C131 - C133 - C134	70.8(2.1)
Molecule 2	
Ni2 - N22 - C221 - C222	-158.0(1.3)
Ni2 - N22 - C221 - C223	86.6(1.5)
N22 - C221 - C223 - C224	-123.1(1.7)
Ni2 - N23 - C231 - C232	24.6(4.7)
Ni2 - N23 - C231 - C233	-152.2(2.1)
N23 - C231 - C233 - C234	-122.4(2.8)

TABLE 3.23 WEIGHTED LEAST SQUARES PLANES

Equations of least-squares planes are expressed in orthogonal space as: M1×X + M2×Y + M3×Z = D

Molecule 1

Plane 1 : The phenyl group C123, C124, C125, C126, C127, C128

M1 = -.7087(57)

M2 = -.5642(68)

M3 = -.4235(75)

D = -16.5104(413)

Sum of $(D/S)^2$ for the atoms in this ring = 4.57

Chi-squared at 95% for 3 degrees of freedom = 7.81

The group of atoms does not deviate significantly from planarity.

Plane 2 : The phenyl group C133, C134, C135, C136, C137, C138

M1 = .6598(57)

M2 = -.4321(75)

M3 = -.6147(61)

D = -.3239(1305)

Sum of $(D/S)^2$ for the atoms in this ring = 6.65

Chi-squared at 95% for 3 degrees of freedom = 7.81

The group of atoms does not deviate significantly from planarity.

Molecule 2

Plane 3 : The phenyl ring C223, C224, C225, C226, C227, C228

M1 = .3095(78)

M2 = .8816(39)

M3 = -.3564(85)

D = -1.6572(1186)

Sum of $(D/S)^2$ for the atoms in this ring = 3.20

Chi-squared at 95% for 3 degrees of freedom = 7.81

The group of atoms does not deviate significantly from planarity.

Plane 4 : The phenyl group C233, C234, C235, C236, C237, C238

M1 = -.1247(82)

M2 = .7881(46)

M3 = -.6028(60)

D = 5.7004(1234)

Sum of $(D/S)^2$ for the atoms in this ring = 2.69

Chi-squared at 95% for 3 degrees of freedom = 7.81

The group of atoms does not deviate significantly from planarity.

b) The Crystal and Molecular Structure of $[Ni(NCS)_2((S)$-α-Phenylethylamine$)_4]$ in Triclinic P1

i) The Unit Cell and Intensity Data Collection

Attempts were made to obtain clathrates with the host complex made from pure (*d*)- or (*l*)-α-phenylethylamine. Some crystals obtained from a methanol and *sec*-butylbenzene solution of the (*l*)-clathrate material gave rise to a triclinic cell, when reflections found by the automatic peak search routine of the diffractometer were indexed.

The cell found was:

a = 11.641(4)Å	b = 11.697(4)Å	c = 14.868(9)Å
α = 71.28(5)°	β = 71.28(5)°	γ = 84.61(3)°

It contains a volume of 1820.8(1.6)Å^3. This corresponds to two host molecules per unit cell, but the volume per host molecule here is ≈910Å^3, compared to ≈880Å^3 in the host structures described earlier.

The cell found above was treated with great suspicion, as the similar values of a and b aswell as α and β are usually indicative of higher symmetry, i.e. a monoclinic or higher-symmetry space-group. The Niggli-values for the cell are:

135.5034	136.8219	221.0552
55.8151	54.2380	12.7841

Possible transformations indicated were:

1) to an A-centered monoclinic cell: (D=0.407)

a = 14.868Å	b = 15.708Å	c = 17.226Å
α = 89.724°	β = 115.393°	γ = 90.389°

by the transformation matrix:

$$\begin{pmatrix} 0 & 0 & -1 \\ -1 & 1 & 0 \\ 1 & 1 & 0 \end{pmatrix}$$

2) to a triclinic cell:

$a = 11.641\text{Å}$ $\quad b = 11.697\text{Å}$ $\quad c = 14.868\text{Å}$

$\alpha = 90.00^{\circ}$ $\quad \beta = 108.26^{\circ}$ $\quad \gamma = 95.39^{\circ}$

by the transformation matrix:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

The required equivalences in the data transformed, $|F(hkl)| = |F(h\bar{k}l)|$ for monoclinic (unique axis b), were not observed, and the cell can only be termed pseudo-monoclinic. The second transformation gives another equal-volumed triclinic cell, which contains no additional symmetry information.

Intensity data were thus collected in the triclinic cell originally found. Because the structure contains only one ligand-enantiomer, the space-group can only be acentric P1. Data were collected for $1^{\circ} < \theta < 24^{\circ}$. Three standard reflections periodically monitored during the data collection were stable to within 3.7% of their mean value. Bijvoet pairs were not collected, as the absolute structure could be inferred from the results obtained for the (*d*)-α-phenylethylamine complex structure, reported in Section 3.2.2a.

Accurate cell parameters determined by least-squares analysis on 25 reflections in the θ-range 15° - 16° and other relevant crystal data are listed in Table 3.24.

TABLE 3.24 CRYSTAL DATA

Molecular Formula	$C_{34}H_{44}N_6NiS_2$
Molecular Weight	$659.59 gmol^{-1}$
Space-Group	P1
a	11.641(4)Å
b	11.697(4)Å
c	14.868(9)Å
α	$71.28(5)^\circ$
β	$71.74(4)^\circ$
γ	$84.61(3)^\circ$
Volume	$1820(2)Å^3$
Z	2
D_c	$1.20 gcm^{-3}$
$\mu(MoK_\alpha)$	$5.74 mm^{-1}$
F(000)	700
Crystal Dimensions	0.45 x 0.40 x 1.12mm
Scan mode	$\omega-2\theta$
Scan width	$(1.44+0.35\tan\theta)^\circ$
Vertical aperture length	4mm
Aperture width	$(1.37+1.05\tan\theta)$mm
Final acceptance limit	20σ at $20^\circ min^{-1}$ in ω
Maximum recording time	40s
Crystal stability	3.7%
Range scanned	$1 - 20^\circ\theta$
Total number of reflections	5945
Final Refinement Data	
R	0.084
R_w	0.077
S	7.72
N	3703
NP	383

ii) Solution and Refinement of the Structure

The phasing difficulties discussed in the orthorhombic host structures were even more severely experienced in this triclinic structure. An attempt at direct phasing using SHELXS-84 was unsuccessful. The structure was eventually solved by the heavy atom method.

The Patterson map calculated for the 3702 unique reflections with $I_{rel} > 2\sigma I_{rel}$ gave highest peaks in the following positions:

Peak	*x/a*	*y/b*	*z/c*	*Rel.Intensity*	
1	.000	.000	.000	1000	
2	.006	.005	.500	433	Ni×Ni
3	.005	.005	.337	198	
4	.005	.995	.663	198	
5	.721	.017	.361	164	
6	.279	.983	.684	164	S×Ni
7	.045	.275	.163	162	
8	.995	.725	.837	162	S×Ni
9	.023	.255	.675	140	
10	.977	.745	.325	140	S×Ni
11	.261	.957	.194	140	
12	.739	.043	.806	140	S×Ni

These peaks correspond to Ni×Ni and Ni×S vectors. One non-origin peak of greater intensity than all the others (Peak 2) allows the positioning of the two Ni atoms at (0.0, 0.0, 0.0) and (0.0, 0.0, 0.5) approximately. On placing the nickel atoms and carrying out Fourier summations, however, no sensible phasing information was obtained (R=0.37), and the location of the sulphur atoms had to be sought from the Patterson map.

In addition, the strong peaks 3 and 4 at ≃(0.0, 0.0, 0.33) and (0.0, 0.0, 0.66) caused some confusion, as they

appeared to indicate an atom on the z-axis between the two nickel atoms. Moreover, no immediate clues could be derived from the centrosymmetric peaks (5&6, 7&8, 9&10, 11&12), because they all are approximately equidistant from both nickel positions!

Inclusion of any four sulphur atoms in non-inversion-center-related positions revealed typically one amine ligand, one or two further phenyl groups, and twelve peaks at Ni-N distances around each nickel atom (R=0.35). As before, subsequently inserted carbon atoms, as for example phenyl groups, were moved into totally unrecognizable geometries during the next L.S. cycles.

Initial phasing was by trial-and-error placing of the sulphur atoms in four of the eight positions indicated by the Patterson peaks, and the positional fixing of any atom groups apparent in a Fourier map. When the equivalent of four out of eight complete amine ligands had been placed, the residual was R = 0.23. Even at this stage it was still unclear which sulphur atoms belonged to which of the two molecules, as electron-density peaks corresponding to nitrogen and carbon atoms appeared between each sulphur atom and both nickel atoms. The positions of remaining atoms remained obscure even when most atoms were placed, and the residual remained above R = 0.22 until all atoms were included in the model. Only when all non-hydrogen atoms were included and the nickel and sulphur atoms treated anisotropically did the residual drop to R = 0.092.

Finally, when hydrogen atoms of parent carbon atoms were placed in calculated positions, a weighting scheme $1/\sigma^2 F$ was introduced and the nickel atoms treated anisotropically,

the weighted residual was $R_w = 0.077$[¶].

The structure was solved with positive complex scattering factors for all atoms, (+f''), and inspection of the conformation of the α-C atoms revealed that they all had the (*S*)-configuration.This, being the opposite absolute configuration to the host complex with (*d*)-α-phenylethylamine ligands which was shown to correspond to the (*R*)-configuration, was taken as correct.

Positional and thermal atomic parameters are listed in Table 3.25. Observed and calculated structure factors are shown in Appendix 8.

From the atomic coordinates of the solved structure, the appearance of the Patterson peaks 3 and 4 at (0.0, 0.0, 0.33) and (0.0, 0.0, 0.66) can be explained:

Atom	*x/a*	*y/b*	*z/c*	*Patterson peaks*		
S11	.075	.238	-.343	.024	.036	.332
C141	.051	.274	-.011	.015	.023	.341
C261	.036	.251	.352	.039	.013	.305
S12	-.031	-.276	-.169	.037	.028	.332
C161	.006	-.248	.163	.085	.010	.368
C241	-.079	-.286	.531	.048	.010	.300

Similar fortuitously related positions are observed between S21, C151, C231 and S22, C131, C251 respectively. The additive S×C and C×C vectors may thus give rise to the observed, strong Patterson peaks.

[¶]*Owing to the large number of parameters required to describe the two independent molecules and the limitations of the refinement program, the sulphur atoms were not treated anisotropically in the final refinements.*

iii) Description of the Structure

Molecular Structure

Perspective views of the two independent molecules, showing atomic nomenclature, appear in Fig.3.32. Molecular bond distances and bond angles are listed in Tables 3.26 and 3.27 respectively. Selected torsion angles appear in Table 3.28.

As born out by bond distances, angles and torsion angles, the molecular structures of the two molecules correspond closely to the inverse of 'Molecule 1' in the host structure described above (3.2.2a). Distortions of bond lengths and angles, especially of the phenyl groups, are expected to be a result of interference by a pseudo-symmetry element in the structure-factor calculation or a result of a degree of disorder, and not owing to steric constraints peculiar to the molecular packing in this structure. Whereas the nickel complex molecules in all the structures described earlier possess an element of symmetry (a two-fold axis or an inversion center), the nickel atoms in this structure do not fall on positions with site-symmetry greater than 1. The absence of a two-fold axis in these host molecules is most evident in the difference between the two Ni-N-CS bond angles of Molecule 2, which are 171 and 153^{o} respectively (161 and 166^{o} in Molecule 1).

Comparing the two independent molecules by considering the differences of their orthogonal internal coordinates after 'superimposing' the atomic sets by a L.S. rotation- and translation vector gave the following results:

(obtained by the program PARST)

Orthogonal coordinates	$\Sigma(D/S)^2$
x	44.68
y	84.41
z	604.73

Chi-squared at 95% for 43 degrees of freedom = 59.30. The two molecules therefore differ significantly from each other.

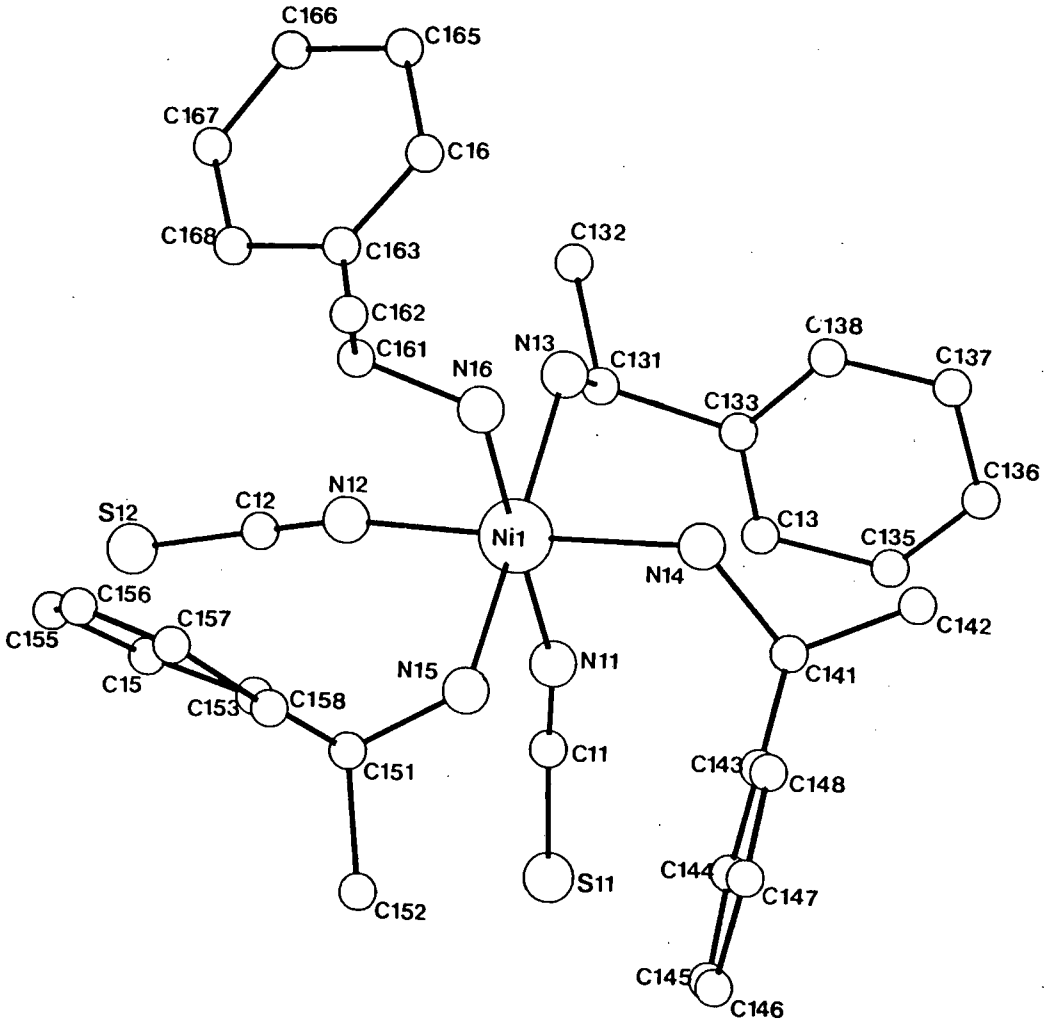
Molecular Packing

Illustrations of the packing are shown in projections along (010) and (001) in Figs.3.33a and 3.33b respectively.

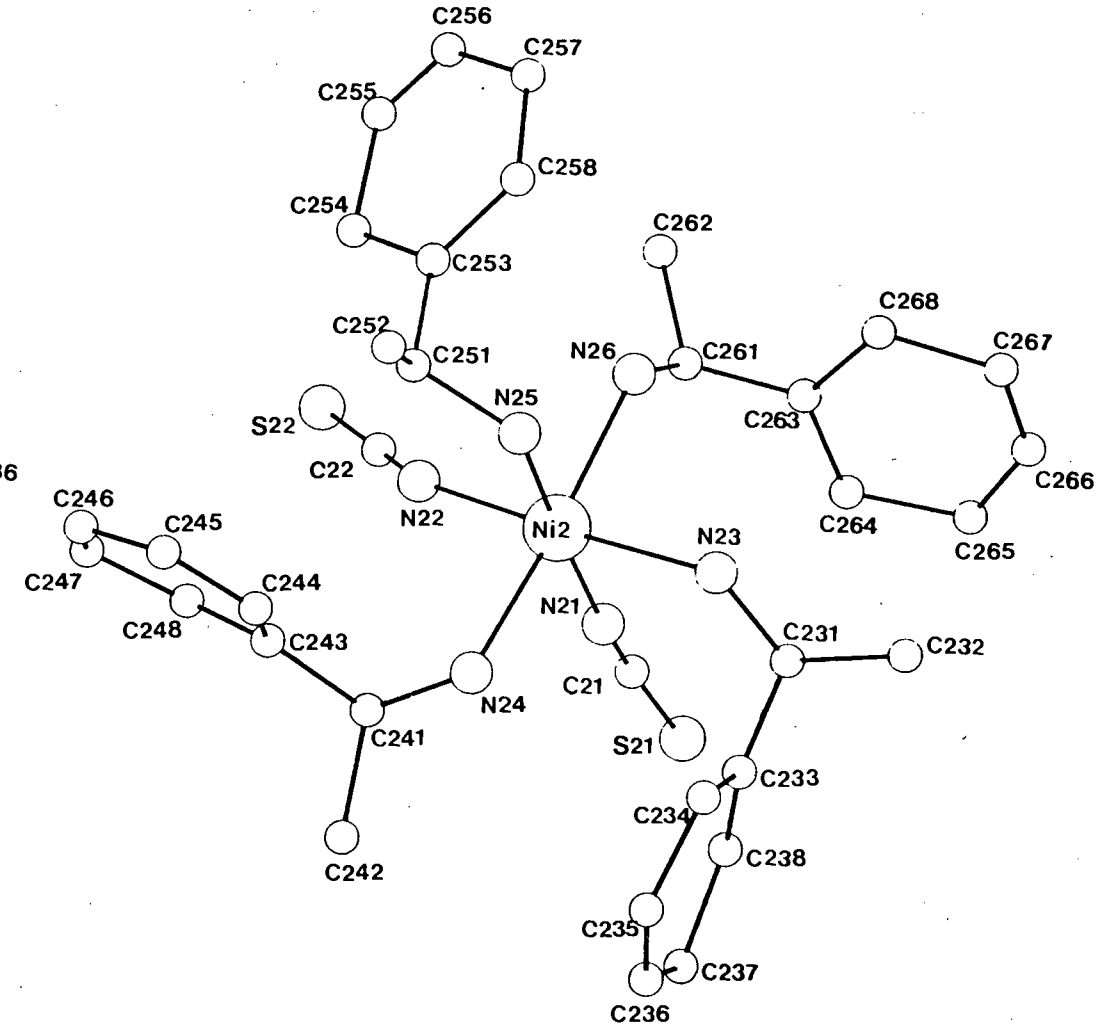
The structure consists of discrete molecules of $[Ni(NCS)_2((S)$-α-phenylethylamine$)_4]$. They are stacked in columns down (001) at intervals of ≃7.5Å, forming a pseudo-screw axis along this direction. As the -NCS groups of consecutive molecules are 90^o to each other (see Fig. 3.33a), a four-fold screw axis would have to be formed. This, however, would require individual molecules to have 2-fold symmetry. Although such symmetry has been observed in the orthorhombic structures reported earlier, it is not quite observed here, resulting in a highly pseudo-symmetrical structure.

The main difference between this host structure and the orthorhombic structures discussed earlier is that in this triclinic structure, alternate columns of molecules down (001) have the molecules pointing in the same direction. I.e. the isothiocyanate groups of all the molecules are situated on the same side of the nickel atoms, whereas in

the orthorhombic structures alternate columns have molecules pointing in opposite directions. The resulting structure is somewhat less efficiently packed than the orthorhombic host structures.

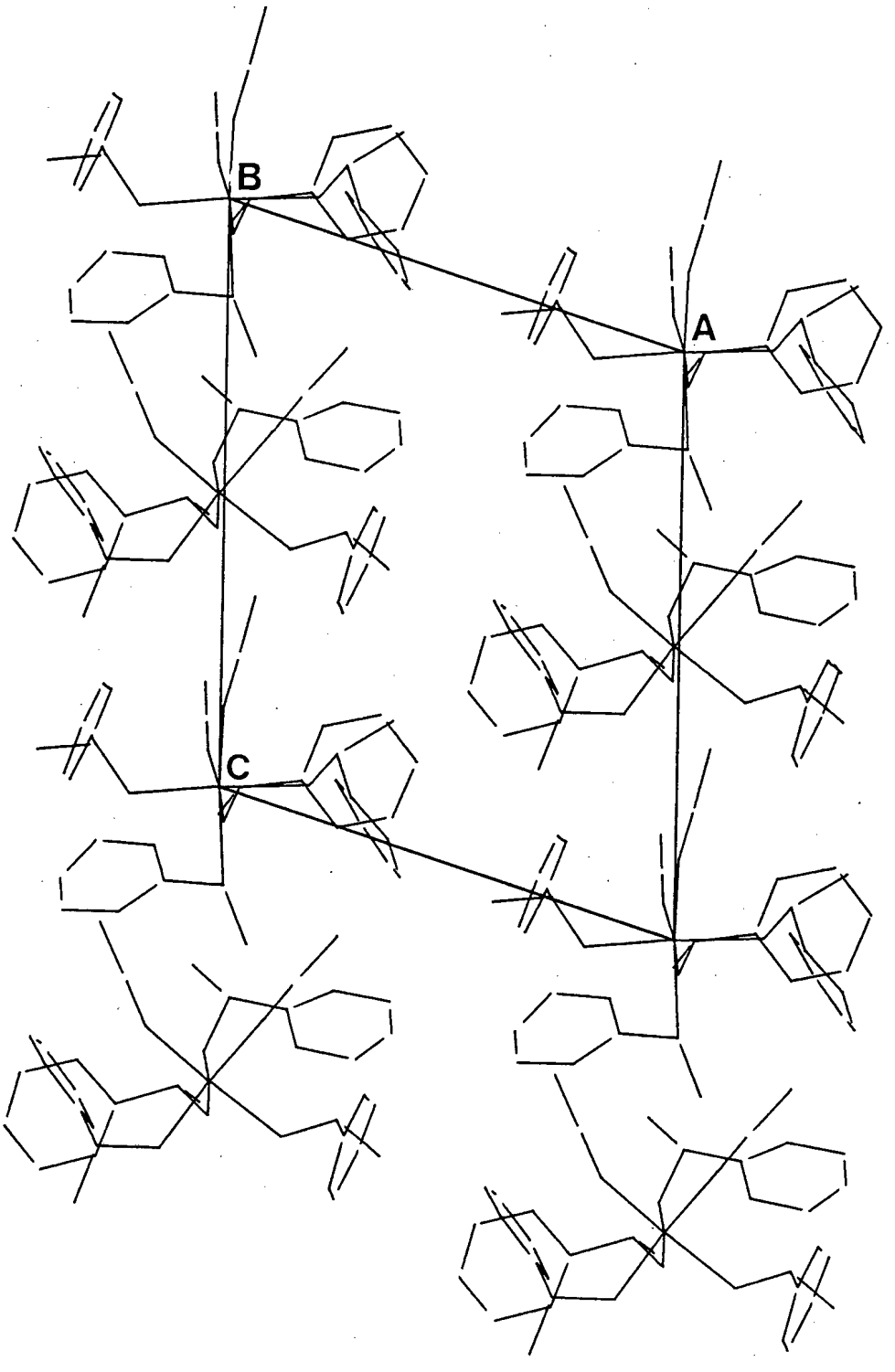


(a) Perspective view of Molecule 1



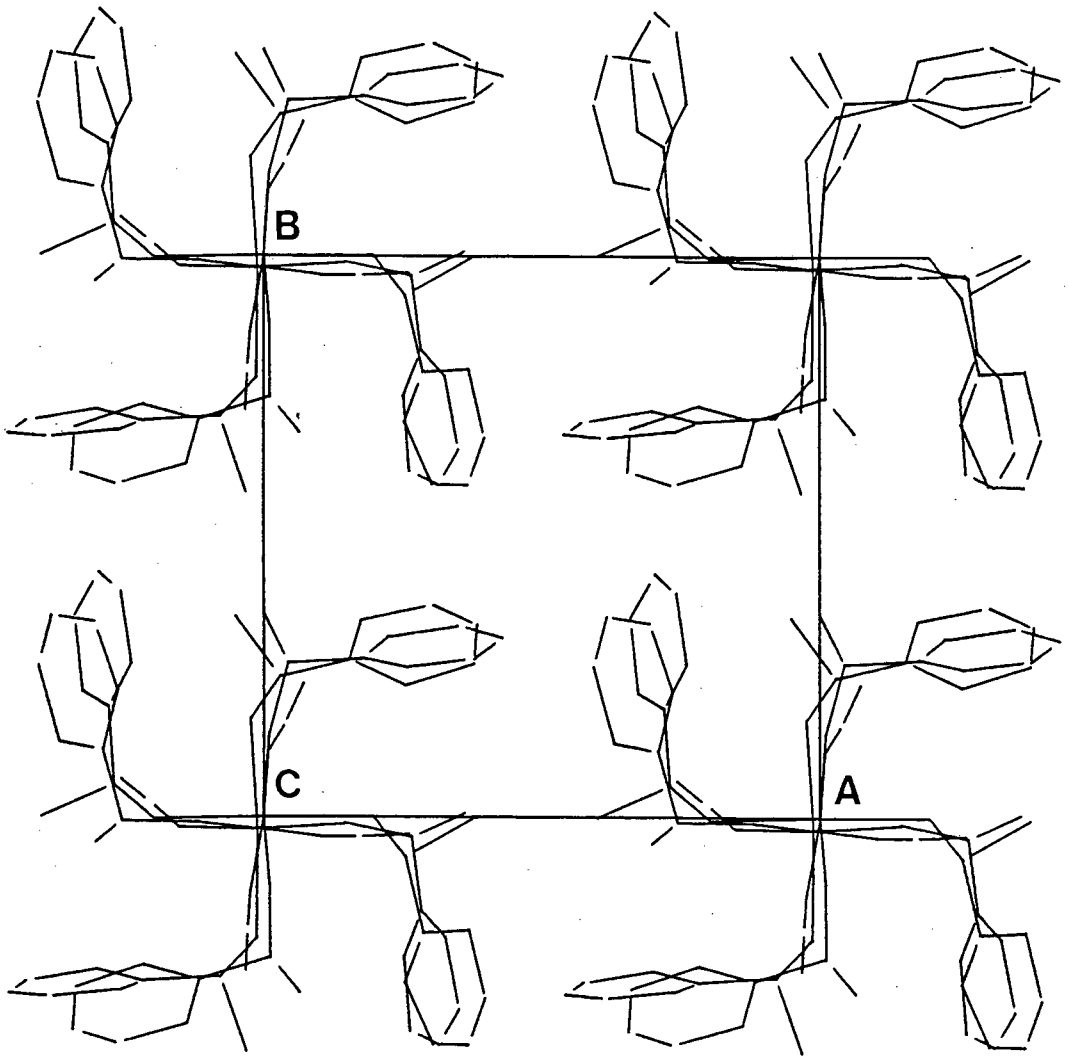
(b) Perspective view of Molecule 2

Figure 3.32



(a) Molecular packing : View down the y axis

Figure 3.33



(b) Molecular packing : View down the *z* axis

Figure 3.33

TABLE 3.25 FRACTIONAL ATOMIC PARAMETERS AND THERMAL PARAMETERS ($U_{ij} \times 10^3$)

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
Molecule 1				
Ni1	.0000	.0000	.0000	a
N11	.0061(13)	.1156(12)	-.1362(11)	66(5)
C11	.0357(15)	.1612(16)	-.2179(14)	66(5)
S11	.0745(5)	.2377(5)	-.3432(5)	92(2)
N12	-.0209(13)	-.1345(13)	-.0539(11)	70(5)
C12	-.0272(14)	-.1907(14)	-.1014(12)	57(5)
S12	-.0311(5)	-.2757(5)	-.1694(4)	81(2)
N13	-.1915(12)	-.0079(11)	.0646(10)	59(4)
C131	-.2731(16)	.0555(15)	.0011(14)	74(6)
H631	-.2374(16)	.0489(15)	-.0676(14)	200(56)
C132	-.3959(18)	-.0072(18)	.0459(16)	104(7)
H632	-.4223(18)	.0411(18)	-.0131(16)	102(17)
H633	-.4686(18)	-.0346(18)	.1053(16)	102(17)
H634	-.3497(18)	-.0792(18)	.0317(16)	102(17)
C133	-.2807(14)	.1955(13)	-.0132(12)	50(4)
C134	-.2429(16)	.2710(17)	-.1006(14)	76(6)
H134	-.2095(16)	.2453(17)	-.1617(14)	172(22)
C135	-.2524(22)	.3966(23)	-.1039(20)	127(9)
H135	-.2180(22)	.4588(23)	-.1697(20)	172(22)
C136	-.3013(20)	.4347(21)	-.0284(19)	117(8)
H136	-.3100(20)	.5229(21)	-.0363(19)	172(22)
C137	-.3415(18)	.3486(19)	.0656(16)	93(7)
H137	-.3801(18)	.3729(19)	.1270(16)	172(22)
C138	-.3272(16)	.2281(17)	.0701(14)	74(6)
H138	-.3511(16)	.1641(17)	.1363(14)	172(22)
N14	.0122(12)	.1453(11)	.0592(10)	60(4)

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
C141	.0506(17)	.2740(16)	-.0112(14)	78(6)
H641	.0165(17)	.2952(16)	-.0683(14)	200(56)
C142	-.0020(19)	.3567(18)	.0499(15)	104(7)
H642	.0066(19)	.4451(18)	.0131(15)	102(17)
H643	.0393(19)	.3369(18)	.1027(15)	102(17)
H644	-.0897(19)	.3349(18)	.0814(15)	102(17)
C143	.1815(16)	.2854(15)	-.0597(14)	66(5)
C144	.2284(18)	.3203(17)	-.1609(15)	84(6)
H144	.1706(18)	.3323(17)	-.2007(15)	172(22)
C145	.3438(20)	.3389(18)	-.2104(18)	101(7)
H145	.3721(20)	.3644(18)	-.2848(18)	172(22)
C146	.4276(23)	.3193(20)	-.1532(19)	123(9)
H146	.5165(23)	.3325(20)	-.1869(19)	172(22)
C147	.3807(20)	.2831(18)	-.0465(17)	103(7)
H147	.4368(20)	.2675(18)	-.0050(17)	172(22)
C148	.2594(17)	.2688(16)	-.0030(15)	77(6)
H148	.2267(17)	.2461(16)	.0712(15)	172(22)
N15	.1955(12)	.0013(12)	-.0547(10)	63(4)
C151	.2523(16)	-.0676(15)	-.1242(13)	69(5)
H651	.1957(16)	-.0753(15)	-.1605(13)	200(56)
C152	.3701(19)	-.0024(21)	-.2018(17)	121(8)
H652	.4105(19)	-.0573(21)	-.2417(17)	102(17)
H653	.4280(19)	.0189(21)	-.1721(17)	102(17)
H654	.3442(19)	.0729(21)	-.2460(17)	102(17)
C153	.2861(17)	-.1891(18)	-.0644(14)	78(6)
C154	.2527(19)	-.2881(19)	-.0783(16)	100(7)
H154	.2024(19)	-.2814(19)	-.1233(16)	172(22)
C155	.2956(21)	-.4086(22)	-.0240(18)	117(8)
H155	.2758(21)	-.4842(22)	-.0339(18)	172(22)

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
C156	.3605(26)	-.4129(27)	.0390(22)	160(12)
H156	.3810(26)	-.4950(27)	.0779(22)	172(22)
C157	.3958(22)	-.3265(24)	.0514(20)	132(9)
H157	.4409(22)	-.3385(24)	.1009(20)	172(22)
C158	.3709(21)	-.1985(22)	-.0100(17)	121(8)
H158	.4115(21)	-.1257(22)	-.0121(17)	172(22)
N16	.0075(11)	-.1169(11)	.1450(10)	53(4)
C161	.0061(16)	-.2479(15)	.1627(13)	64(5)
H661	.0532(16)	-.2720(15)	.1028(13)	200(56)
C162	.0559(22)	-.3007(22)	.2500(17)	136(9)
H662	.0307(22)	-.3874(22)	.2741(17)	102(17)
H663	.0352(22)	-.2685(22)	.3078(17)	102(17)
H664	.1451(22)	-.2937(22)	.2165(17)	102(17)
C163	-.1250(18)	-.2907(17)	.1919(15)	78(6)
C164	-.2105(21)	-.2609(19)	.2657(17)	109(8)
H164	-.1910(21)	-.2095(19)	.3013(17)	172(22)
C165	-.3329(25)	-.3057(23)	.2902(20)	148(10)
H165	-.4017(25)	-.2854(23)	.3428(20)	172(22)
C166	-.3508(33)	-.3846(30)	.2362(27)	202(16)
H166	-.4330(33)	-.4207(30)	.2562(27)	172(22)
C167	-.2660(24)	-.4088(23)	.1596(20)	132(9)
H167	-.2861(24)	-.4556(23)	.1208(20)	172(22)
C168	-.1471(22)	-.3665(20)	.1387(17)	119(8)
H168	-.0789(22)	-.3889(20)	.0869(17)	172(22)
Molecule 2				
Ni2	-.0118(2)	-.0212(2)	.5036(2)	a
N21	.1006(13)	-.0384(13)	.3737(12)	69(5)
C21	.1589(16)	-.0335(15)	.2983(15)	68(5)
S21	.2657(5)	-.0308(5)	.1863(4)	77(2)

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
N22	-.1508(15)	-.0183(14)	.4457(13)	87(6)
C22	-.1946(16)	.0143(16)	.3856(15)	72(6)
S22	-.2544(6)	.0696(6)	.2931(5)	116(2)
N23	.1443(13)	-.0108(12)	.5602(10)	57(4)
C231	.2601(1)	-.0350(17)	.5015(14)	79(6)
H731	.2616(17)	.0078(17)	.4311(14)	200(92)
C232	.3646(21)	.0058(21)	.5288(18)	130(9)
H732	.3356(21)	.0909(21)	.5177(18)	102(18)
H733	.4526(21)	.0055(21)	.4915(18)	102(18)
H734	.3525(21)	-.0344(21)	.6015(18)	102(18)
C233	.2806(15)	-.1701(15)	.5222(13)	60(5)
C234	.2498(15)	-.2529(16)	.6236(14)	75(6)
H234	.2222(15)	-.2207(16)	.6815(14)	172(22)
C235	.2592(18)	-.3800(19)	.6402(16)	92(7)
H235	.2328(18)	-.4407(19)	.7079(16)	172(22)
C236	.3071(20)	-.4130(21)	.5537(18)	116(8)
H236	.3127(20)	-.5018(21)	.5637(18)	172(22)
C237	.3531(20)	-.3383(21)	.4525(18)	110(8)
H237	.3944(20)	-.3697(21)	.3953(18)	172(22)
C238	.3303(18)	-.2141(19)	.4434(17)	100(7)
H238	.3517(18)	-.1550(19)	.3748(17)	172(22)
N24	-.0115(12)	-.2144(11)	.5621(10)	53(4)
C241	-.0795(15)	-.2858(15)	.5312(13)	66(5)
H741	-.0725(15)	-.2435(15)	.4595(13)	200(92)
C242	-.0274(17)	-.4159(16)	.5403(14)	84(6)
H742	.0570(17)	-.3848(16)	.5038(14)	102(18)
H743	-.0498(17)	-.4681(16)	.5066(14)	102(18)
H744	-.0326(17)	-.4642(16)	.6105(14)	102(18)

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
C243	-.2091(15)	-.2949(14)	.5963(12)	54(5)
C244	-.2593(17)	-.3143(16)	.6989(14)	77(6)
H244	-.2017(17)	-.3177(16)	.7374(14)	172(22)
C245	-.3810(19)	-.3293(17)	.7499(16)	89(7)
H245	-.4112(19)	-.3469(17)	.8238(16)	172(22)
C246	-.4569(17)	-.3182(16)	.6963(14)	71(6)
H246	-.5451(17)	-.3295(16)	.7333(14)	172(22)
C247	-.4263(18)	-.2943(17)	.6007(15)	84(6)
H247	-.4896(18)	-.2881(17)	.5668(15)	172(22)
C248	-.3066(18)	-.2774(16)	.5461(15)	86(6)
H248	-.2841(18)	-.2525(16)	.4718(15)	172(22)
N25	-.1161(13)	-.0067(12)	.6456(10)	61(4)
C251	-.2485(17)	-.0031(17)	.6750(15)	77(6)
H751	-.2770(17)	-.0589(17)	.6475(15)	200(92)
C252	-.2978(20)	-.0436(21)	.7848(16)	121(8)
H752	-.3836(20)	-.0172(21)	.7925(16)	102(18)
H753	-.2571(20)	.0057(21)	.8101(16)	102(18)
H754	-.2961(20)	-.1308(21)	.8237(16)	102(18)
C253	-.2928(17)	.1160(17)	.6317(14)	75(6)
C254	-.3618(20)	.1400(21)	.5686(17)	113(8)
H254	-.3857(20)	.0687(21)	.5555(17)	172(22)
C255	-.4037(23)	.2577(25)	.5184(20)	148(10)
H255	-.4525(23)	.2679(25)	.4717(20)	172(22)
C256	-.3690(25)	.3558(26)	.5417(21)	146(11)
H256	-.3980(25)	.4381(26)	.5110(21)	172(22)
C257	-.3024(19)	.3441(21)	.6033(17)	109(8)
H257	-.2770(19)	.4159(21)	.6154(17)	172(22)
C258	-.2674(18)	.2186(19)	.6500(16)	100(7)
H258	-.2223(18)	.2066(19)	.6995(16)	172(22)

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
N26	-.0259(13)	.1759(13)	.4571(12)	76(5)
C261	.0361(17)	.2510(16)	.3520(14)	77(6)
H761	.0472(17)	.2045(16)	.3040(14)	200(92)
C262	-.0475(23)	.3612(21)	.3191(21)	166(12)
H762	.0054(23)	.4110(21)	.2532(21)	102(18)
H763	-.0624(23)	.4062(21)	.3686(21)	102(18)
H764	-.1263(23)	.3445(21)	.3120(21)	102(18)
C263	.1578(20)	.2781(18)	.3396(16)	90(7)
C264	.2571(25)	.2311(22)	.2828(19)	132(9)
H264	.2478(25)	.1698(22)	.2517(19)	172(22)
C265	.3745(27)	.2777(24)	.2709(21)	141(11)
H265	.4478(27)	.2564(24)	.2224(21)	172(22)
C266	.388 (29)	.3405(26)	.3191(23)	155(12)
H266	.4722(29)	.3684(26)	.3052(23)	172(22)
C267	.3108(28)	.3728(24)	.3783(22)	147(11)
H267	.3347(28)	.4089(24)	.4225(22)	172(22)
C268	.1767(29)	.3578(26)	.3898(22)	172(12)
H268	.1093(29)	.3990(26)	.4283(22)	172(22)

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a

Anisotropic thermal parameters ($U_{ij} \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni1	56(1)	50(1)	52(1)	-18(1)	-20(1)	4(1)
Ni2	55(1)	47(1)	52(1)	-9(1)	-23(1)	-4(1)

TABLE 3.26 BOND DISTANCES (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Molecule 1		*Molecule 2*	
Ni1 - N11	2.026(14)	Ni2 - N21	2.025(16)
Ni1 - N12	2.044(18)	Ni2 - N22	2.050(21)
Ni1 - N13	2.131(13)	Ni2 - N23	2.256(18)
Ni1 - N14	2.183(16)	Ni2 - N24	2.145(12)
Ni1 - N15	2.163(13)	Ni2 - N25	2.132(14)
Ni1 - N16	2.175(13)	Ni2 - N26	2.190(15)
N11 - C11	1.111(23)	N21 - C21	1.100(25)
C11 - S11	1.719(19)	C21 - S21	1.731(19)
N12 - C12	1.130(28)	N22 - C22	1.111(30)
C12 - S12	1.642(21)	C22 - S22	1.655(24)
N13 - C131	1.524(25)	N23 - C231	1.417(22)
C131 - C132	1.520(27)	C231 - C232	1.554(38)
C131 - C133	1.580(24)	C231 - C233	1.521(26)
C133 - C134	1.281(21)	C233 - C234	1.459(23)
C133 - C138	1.348(28)	C233 - C238	1.371(32)
C134 - C135	1.449(35)	C234 - C235	1.426(29)
C135 - C136	1.287(41)	C235 - C236	1.394(37)
C136 - C137	1.401(29)	C236 - C237	1.433(30)
C137 - C138	1.386(31)	C237 - C238	1.422(33)
N14 - C141	1.544(20)	N24 - C241	1.461(28)
C141 - C142	1.497(31)	C241 - C242	1.565(25)
C141 - C143	1.466(25)	C241 - C243	1.496(22)
C143 - C144	1.364(27)	C243 - C244	1.438(25)
C143 - C148	1.383(33)	C243 - C248	1.482(31)
C144 - C145	1.314(28)	C244 - C245	1.379(26)
C145 - C146	1.442(42)	C245 - C246	1.336(35)

Molecule 1		*Molecule 2*	
C146 - C147	1.437(34)	C246 - C247	1.293(29)
C147 - C148	1.358(28)	C247 - C248	1.371(26)
N15 - C151	1.470(25)	N25 - C251	1.465(24)
C151 - C152	1.560(25)	C251 - C252	1.479(29)
C151 - C153	1.506(25)	C251 - C253	1.456(26)
C153 - C154	1.350(35)	C253 - C254	1.366(36)
C153 - C158	1.437(37)	C253 - C258	1.389(35)
C154 - C155	1.509(31)	C254 - C255	1.460(34)
C155 - C156	1.363(48)	C255 - C256	1.425(49)
C156 - C157	1.212(49)	C256 - C257	1.343(44)
C157 - C158	1.538(34)	C257 - C258	1.488(30)
N16 - C161	1.470(22)	N26 - C261	1.505(21)
C161 - C162	1.514(33)	C261 - C262	1.583(31)
C161 - C163	1.535(28)	C261 - C263	1.423(32)
C163 - C164	1.346(30)	C263 - C264	1.385(33)
C163 - C168	1.449(39)	C263 - C268	1.436(47)
C164 - C165	1.460(38)	C264 - C265	1.457(45)
C165 - C166	1.468(57)	C265 - C266	1.228(53)
C166 - C167	1.342(44)	C266 - C267	1.174(43)
C167 - C168	1.420(39)	C267 - C268	1.537(48)
All C - H bond lengths[a]		1.00 Å	

[a]Bond lengths fixed

TABLE 3.27 ESTIMATED BOND ANGLES (DEGREES) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Molecule 1	*n=2*	*n=3*	*n=4*	*n=5*	*n=6*
N11 - Ni1 - N1*n*	86.6(.6)	97.9(.6)	93.1(.6)	86.2(.6)	175.2(.6)
N12 - Ni1 - N1*n*		86.4(.6)	177.0(.6)	94.7(.6)	96.5(.6)
N13 - Ni1 - N1*n*			90.7(.5)	175.8(.5)	86.0(.5)
N14 - Ni1 - N1*n*				88.2(.6)	84.1(.5)
N15 - Ni1 - N1*n*					89.8(.5)
Ni1 - N11 - C11	161.4(1.6)				
N11 - C11 - S11	176.6(1.8)				
Ni1 - N12 - C12	166.1(1.5)				
N12 - C12 - S12	177.5(1.7)				
Ni1 - N1*n* - C1*n*1		120.0(1.1)	120.7(1.0)	117.4(1.1)	117.4(1.0)
N1*n* - C1*n*1- C1*n*2		109.1(1.5)	105.7(1.5)	110.2(1.6)	104.2(1.6)
N1*n* - C1*n*1- C1*n*3		111.7(1.5)	112.5(1.6)	107.5(1.4)	109.2(1.5)
C1*n*2- C1*n*1- C1*n*3		113.4(1.6)	115.4(1.7)	108.4(1.7)	109.8(1.7)
C1*n*1- C1*n*3- C1*n*8		116.5(1.5)	119.9(1.8)	120.6(2.0)	116.2(1.8)
C1*n*1- C1*n*3- C1*n*4		119.9(1.6)	121.2(1.9)	117.8(1.8)	119.9(2.0)
C1*n*4- C1*n*3- C1*n*8		123.7(1.8)	118.7(1.9)	120.4(2.1)	124.0(2.2)
C1*n*3- C1*n*4- C1*n*5		114.7(1.9)	125.1(2.1)	117.2(2.0)	117.0(2.2)
C1*n*4- C1*n*5- C1*n*6		125.1(2.5)	117.4(2.2)	119.2(2.5)	117.3(2.6)
C1*n*5- C1*n*6- C1*n*7		117.9(2.5)	118.7(2.4)	125.8(3.0)	124.6(3.3)
C1*n*6- C1*n*7- C1*n*8		117.3(2.0)	119.1(2.2)	119.4(2.7)	116.4(2.8)
C1*n*7- C1*n*8- C1*n*3		121.1(1.8)	121.0(2.0)	116.4(2.2)	120.1(2.2)
Molecule 2					
N21 - Ni2 - N2	86.8(.7)	92.2(.6)	87.4(.6)	174.7(.7)	98.1(.7)
N22 - Ni2 - N2		175.9(.7)	93.9(.6)	98.5(.7)	85.7(.7)
N23 - Ni2 - N2			90.0(.6)	82.6(.5)	90.6(.6)
N24 - Ni2 - N2				91.3(.6)	174.5(.6)
N25 - Ni2 - N2					83.3(.6)

Molecule 2 (continued)	*n=2*	*n=3*	*n=4*	*n=5*	*n=6*
Ni2 - N21 - C21	171.5(1.7)				
N21 - C21 - S21	172.7(1.9)				
Ni2 - N22 - C22	152.6(1.8)				
N22 - C22 - S22	176.7(2.0)				
Ni2 - N2*n* - C2*n*1		115.9(1.2)	119.4(1.1)	121.6(1.2)	121.1(1.2)
N2*n* - C2*n*1- C2*n*2		112.6(1.7)	112.2(1.5)	109.8(1.7)	109.2(1.7)
N2*n* - C2*n*1- C2*n*3		111.0(1.6)	109.7(1.5)	111.9(1.7)	111.4(1.7)
C2*n*2- C2*n*1- C2*n*3		102.7(1.7)	109.0(1.5)	111.5(1.8)	117.1(1.9)
C2*n*1- C2*n*3- C2*n*8		118.8(1.7)	120.0(1.5)	122.8(1.9)	117.4(2.2)
C2*n*1- C2*n*3- C2*n*4		121.5(1.6)	129.4(1.7)	124.5(2.0)	123.4(2.2)
C2*n*4- C2*n*3- C2*n*8		119.7(1.8)	110.6(1.6)	112.7(2.0)	119.2(2.5)
C2*n*3- C2*n*4- C2*n*5		120.0(1.7)	124.3(1.9)	127.4(2.3)	115.7(2.4)
C2*n*4- C2*n*5- C2*n*6		114.3(2.0)	117.2(2.0)	114.3(2.4)	122.9(3.0)
C2*n*5- C2*n*6- C2*n*7		129.5(2.4)	125.7(2.1)	124.2(2.8)	126.0(3.7)
C2*n*6- C2*n*7- C2*n*8		111.4(2.1)	119.6(2.0)	115.6(2.3)	121.4(3.0)
C2*n*7- C2*n*8- C2*n*3		124.4(2.1)	122.1(1.8)	125.8(2.0)	113.0(2.5)

TABLE 3.29 SELECTED TORSION ANGLES

Molecule 1	*Angle*	*E.S.D.*
Ni1 - N13 - C131 - C132	154.33°	(1.26)
Ni1 - N13 - C131 - C133	-79.58°	(1.59)
N13 - C131 - C133 - C134	117.90°	(1.88)
Ni1 - N14 - C141 - C142	155.43°	(1.25)
Ni1 - N14 - C141 - C143	-77.77°	(1.76)
N14 - C141 - C143 - C144	120.99°	(2.00)
Ni1 - N15 - C151 - C152	145.71°	(1.32)
Ni1 - N15 - C151 - C153	-96.36°	(1.50)
N15 - C151 - C153 - C154	130.57°	(1.95)
Ni1 - N16 - C161 - C162	160.58°	(1.29)
Ni1 - N16 - C161 - C163	-51.48°	(2.51)
N16 - C161 - C163 - C168	130.87°	(1.90)
Molecule 2		
Ni2 - N23 - C231 - C232	165.05°	(1.37)
Ni2 - N23 - C231 - C233	-80.40°	(1.67)
N23 - C231 - C233 - C238	135.29°	(1.92)
Ni2 - N24 - C241 - C242	154.81°	(1.19)
Ni2 - N24 - C241 - C243	-83.87°	(1.57)
N24 - C241 - C243 - C248	135.50°	(1.69)
Ni2 - N25 - C251 - C252	156.47°	(1.39)
Ni2 - N25 - C251 - C253	-79.22°	(1.89)
N25 - C251 - C253 - C254	119.06°	(2.29)
Ni2 - N26 - C261 - C262	142.98°	(1.48)
Ni2 - N26 - C261 - C263	-86.23°	(1.87)
N26 - C261 - C263 - C264	111.39°	(2.49)

C H A P T E R 4

CHAPTER 4

CONCLUSION

The $Ni(NCS)_2(\alpha\text{-arylalkylamine})_4$ complexes, with the exception of $Ni(NCS)_2(benzylamine)_4$, form clathrates with various compounds, and it has been reported that the nickel complexes have to be made in the presence of a sufficient concentration of guest compound in order for clathration to occur[42]. The crystal structures of the host complexes and two clathrates of the α-phenylethylamine complex suggest a reason for this phenomenon: in the host complex the -NCS groups are in *cis* positions, but in the clathrates they are *trans* to each other. It may therefore be assumed that clathrate lattices can only form with the *trans* structural isomer.

The molecular shapes of the nickel complexes in the host lattices are similar. The conformation of the molecules in the structure of pure (*d*)-α-phenylethylamine closely resembles that of a molecule with four such (*d*)-amine ligands in the structure containing also one molecule with two (*d*)- and two (*l*)-amine ligands (prepared from the racemic amine). In the molecules containing two ligands of either chirality, the methyl and phenyl substituents of the chiral carbon are simply exchanged, retaining approximately the torsion angles of the rest of the molecule.

Three crystals of the (*dl*)-amine host complex were found to have one molecule with four ligands of one chirality, and one molecule with two ligands each of opposite chirality. During complexation using the racemic amine, not only are molecules

with two ligands of either chirality formed, but also those with ligands of singular chirality. It appears that the bimolecular aggregates $MX_2(+)\text{-}L_2(-)\text{-}L_2$: $MX_2(+)\text{-}L_4$ and its enantiomer, $MX_2(-)\text{-}L_2(+)\text{-}L_2$: $MX_2(-)\text{-}L_4$ are of lower energy and therefore more probable than crystals of only $MX_2(+)\text{-}L_2(-)\text{-}L_2$, $MX_2(+)\text{-}L_4$ or $MX_2(-)\text{-}L_4$, which are diastereomeric with respect to the bimolecular crystals.

$Ni(NCS)_2(subst.pyridine)_4$ complexes can only exist in the *trans* form owing to crowding of the pyridine groups which forces them into a "windmill" configuration. No such steric limitations exist in the α-phenylethylamine complex, and unless in the presence of some other compound the *cis*-complex is formed. This is substantiated by results of an energy calculation of the *trans*-to-*cis* transformation which gave the *cis*-isomer as being more stable by 2 - 3kcal/mol than the *trans*-isomer. Even less crowding occurs in the benzylamine complex which has been reported not to form any clathrates. In this case, the stability of the *cis*-isomer over the *trans*-isomer is expected to be great enough to prevent the formation of the *trans*-isomer and thus clathration. A similar situation is expected to prevent clathration by the pure (*d*)- and pure (*l*)-α-phenylethylamine complexes.

Enantiomerically pure α-phenylpropylamine and higher homologues are not commercially available and no research has yet been done on the nickel bisisothiocyanate complexes of these ligands. The next logical step in the study of these Werner complexes, however, is to determine their *trans* viability. Increased crowding around the nickel may force complexes made with these ligands into the *trans* configuration and enable

clathration of chiral and achiral guest molecules.

The study of TOT-clathrates has described that guest selectivity is highest for compounds which conform to the guest-site symmetry[20]. In the crystal structure of the *sec* -butylbenzene clathrate described here it is seen that the part of the guest molecule which has 2-fold symmetry is not disordered, while extensive disorder is observed for the butyl group. Such disorder requires guest cavities which are less specific towards one enantiomer because they are large enough to accommodate one guest molecule in various conformations and orientations. The selective enclathration of chiral molecules is almost certain to be most efficient in lattices with minimal symmetry elements. Mixed ligand complexes may prove useful in this respect.

An understanding of the reason why the α-phenylethylamine complexes form clathrates only under certain conditions may therefore lead to the synthesis of chiral host complexes with *trans*-isothiocyanates. A cyclic process of enantiomeric separation is envisaged, similar to the "Labofina clathration process" (Figure 1.4), which was pioneered for the separation of isomers of xylene.

The most interesting aspect of the *trans-cis* isomerism is that of host-guest interaction. The ultraviolet spectra of a solution of the guest compounds in the amine have no new peaks over and above those of the amine and electronic interactions before complexation are therefore unlikely. The nmr experiment appears to indicate a solution equilibrium of the *cis*- and *trans*-forms in methanol. If, however, the *cis*-form is more stable and clathrate material was dissolved in methanol to

yield crystals of the clathrate, such an equilibrium seems improbable. In addition, no clathrate is formed by dissolving the *cis*-host complex in methanol and adding a suitable guest compound. Clathration may therefore depend entirely on steric factors during complexation for which the guest compounds are directly responsible. Alternatively, the difference in solubility between the host complex and its clathrate may cause the clathrate (incorporating the *trans* complex) to precipitate rather than the *cis* host complex.

Some new conclusions on the host-guest interactions in Werner clathrates may be achieved by a detailed study of what causes the $Ni(NCS)_2(\alpha\text{-phenylethylamine})_4$ molecule to adopt a *trans*-configuration.

This work has allowed establishment of the suitability of various techniques for clathrate studies.

Given dry, stable unrecrystallized material or stable crystals, microanalysis is a useful technique. However, the application to zeolitic clathrates or unstable complexes and crystals remains problamatical.

The total ion current spectrum obtained by mass spectroscopy may be misleading when a material is to be classified as a clathrate or a host complex. Mass spectra, nevertheless, are illuminating particularly when the identities of ligands or the guest compound are open to question.

Application of the α-phenylethylamine complex to gas chromatography is limited, because the complex does not exist in the *trans*-form unless a clathrate has been formed; in this case it is thermally unstable. If, however, the relative retention times obtained for the host-complex column follow the scale of selective enclathration, gas chromatography will determine

which compounds are suitable as guests and which are likely to be effectively separated by a particular host complex.
A quick method to distinguish a host complex from its clathrate, especially when the crystal lattice of the host alone does not contain any cavities in which guest molecules may be accommodated, is powder X-ray diffractometry. Unrecrystallized material is suitable for this technique.

The *cis-trans* isomerism of the α-phenylethylamine complex was established only by determining crystal structures of the host and clathrate complexes. This method of solid state analysis is therefore of paramount importance. Solid state infrared spectroscopy is a rapid technique which also allows the detection of differences between *cis*- and *trans*-isomers. It is perhaps because such isomerism was entirely unexpected that previous studies using IR spectroscopy were not correctly interpreted. The (*dl*)-amine complex now provides a basis for some detailed studies:

1) Unambiguous assignment of peaks in the nmr spectra at varying temperatures with consequent evaluation of equilibrium coefficients and the heat of isomerization in methanol.
2) Assignment of absorption peaks in the IR-spectra of the complex in *cis*- and *trans*-forms, and the rate of conversion as a Nujol mull.

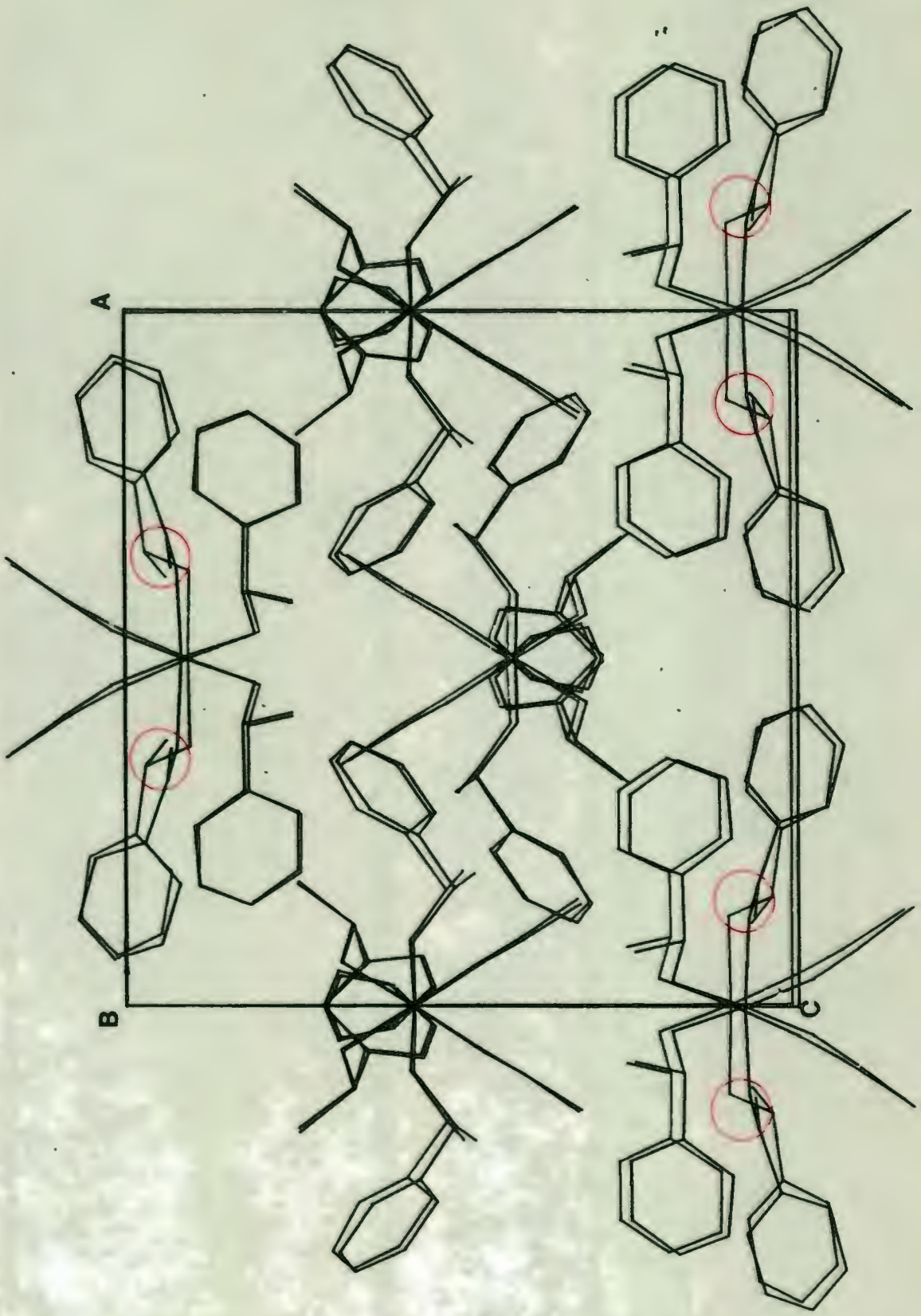


Figure 4.1 Packing diagrams of $Ni(NCS)_2$*RRRR* : $Ni(NCS)_2$*RRRR* (this page) and $Ni(NCS)_2$*RRRR* : $Ni(NCS)_2$*RRSS* (transparency), clearly illustrating the similarity in molecular packing and the inversion of the αC.

Additional Note

After completion of this thesis, a very recent book

Inclusion Compounds : Academic Press Inc.
(London) Ltd.
: 1984

became available. In Chapter 4 a review of the complexes discussed here, aswell as some related complexes, is presented. It includes the work by J.HANOTIER *and* P.de RADZITZKY, *authors of the said chapter, which has been referred to in this work, aswell as some additional conclusions not published before.*

Owing to the indepth crystallographic analyses presented here, this work clarifies many of the erroneous conclusions derived in that publication.

A P P E N D I X 1

NON-CENTROSYMMETRIC STRUCTURES AND THE DETERMINATION OF ABSOLUTE STRUCTURE

APPENDIX 1

NON-CENTROSYMMETRIC STRUCTURES and THE DETERMINATION OF ABSOLUTE STRUCTURE

As this work included several acentric structures requiring the determination of their absolute structures, the study of centric vs. acentric structures and the determination of absolute structures was of special interest.

1) Centric vs. Acentric Structures

Before the problem of having to determine an absolute structure is faced, such a structure will have been found to be acentric. There are many cases in which structures are necessarily acentric, especially when dealing with only one enantiomer of a chiral substance. However, many other cases exist in which acentricity is encountered, and sometimes the classification of a structure as being centric or acentric seems ambiguous.

A first decision on whether a structure is centrosymmetric or not is usually made on inspection of intensity distributions. This is done by an N(z) plot[88] or evaluation of E statistics[89]. The expected results for an N(z) plot are shown in Fig.A-1. A mean $(E^2 - 1)$ statistic of about 0.97 is indicative of centrosymmetrical structures, and one of about 0.74 of non-centrosymmetric structures.

It has been found, however, that deleting weak reflections before making such tests may severely bias the statistics and hence lead to an incorrect space-group assignment[90]. Examples are given in Table A-1.

For true values of intensity statistics the intensities

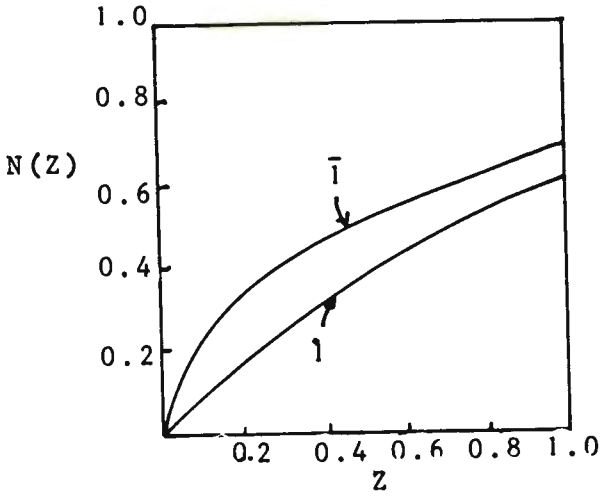


Figure A-1 Theoretical N(Z) curves for centric and acentric structures

of reflections accidentally absent and unobserved should be set to zero, and weak reflections may not be omitted. However, many diffractometers are programmed to skip reflections if the counting rate is low; apart from being a time-saving measure, weak reflections have little importance in Patterson maps, the least squares process and some phasing techniques. Ignoring them also has a cosmetic effect of a lower residual R, which may make the final product more acceptable. The introduction of the goodness-of-fit parameter S, however, will encourage the inclusion of weak reflections in data collections and structure refinements.

Hamilton's significance test[85] has become a popular tool to determine the statistical validity of removing a center from a structure where its existence seems ambiguous. As indicated by Marsh[90], however, the non-centrosymmetric distortion of an approximately centrosymmetric structure shows up only as an out-of-phase component to the structure factor. If this distortion is small, it will be a small scattering vector at right angles to the 'real' vector, owing to the primarily centro-

symmetric nature of such a structure. Therefore, only if the centrosymmetric component of F itself is small, will the out-of-phase component be able to cause a meaningful change in the magnitude of F.

The weak reflections are therefore especially important in distinguishing between a true and an apparent center, and tests made only on the stronger reflections cannot be considered conclusive.

	No.of reflections	$I_{rel} > n\sigma I_{rel}$	$(E^2 - 1)$
a)	2416	0	0.999
	1890	5	0.877
	1561	12	0.790
b)	7936	2	0.922
	2340	2	0.820

Table A-1 Some E statistics for subsets of two data sets, for a) $Cu_8C_{76}H_{99.4}N_{24}O_{13.7}B_4Si_2F_{28}$ [91] and b) $C_{14}H_{15}ONClP$ [92].

2) Absolute Structure Determination

Anomalous dispersion effects in non-centrosymmetric structures can be used to determine[94]:

i) Absolute Configuration

The structure must contain at least one asymmetric center and only one enantiomer. Absolute configuration cannot be determined for non-centric but achiral space-groups (containing, e.g., a mirror or glide plane), and molecules lacking asymmetric centers (achiral).

ii) Absolute Conformation (the sign of all torsion angles)

This is determined for achiral molecules in chiral space-groups.

iii) Polar Axis Direction

For polar space-groups (most achiral non-centrosymmetric space-groups).

iv) Absolute Assignment of X- and Y-Axes

In some achiral non-centrosymmetric space-groups lacking polar axes, e.g. $I\bar{4}$.

v) The Space-Group

For some enantiomorphic pairs of space-groups.

Apart from determining the absolute structure, it is important to notice that possible large systematic errors in heavy-atom positions may be incurred if the structure is refined in the wrong absolute sense[95].

a) Friedel Pairs and Bijvoet Pairs

For centrosymmetric structures the intensities F_o of Friedel opposites are the same:

$$|F_o(hkl)| = |F_o(\bar{h}\bar{k}\bar{l})|$$

When dispersion effects occur, however, the symmetry of $|F_o|$ in reciprocal space degrades from the Laue symmetry to reveal the true point-group. Thus reflections $\{hkl\}$ that are point-group related to hkl all have the same intensity, which differs from that found for all reflections $\{\bar{h}\bar{k}\bar{l}\}$ that are point-group related to $\bar{h}\bar{k}\bar{l}$.

For non-centrosymmetric structures any one pair, one from

$\{hkl\}$, and the other from $\{\bar{h}\bar{k}\bar{l}\}$, constitute a Bijvoet pair and can be used for S_o:I_o[¶] assignment. Any two reflections, on the other hand, from one of the two sets $\{hkl\}$ or $\{\bar{h}\bar{k}\bar{l}\}$ constitute a Friedel pair (not Friedel opposites) with theoretically equivalent intensities.

e.g. $P2_12_12$

$F(hkl)$		$F(\bar{h}\bar{k}\bar{l})$
$F(h\bar{k}\bar{l})$	← Bijvoet pairs →	$F(\bar{h}kl)$ ↑
$F(\bar{h}k\bar{l})$		$F(h\bar{k}l)$ Friedel pairs
$F(\bar{h}\bar{k}l)$		$F(hk\bar{l})$ ↓

b) Determining the Correct Structure

The recommended procedures for the determination of the absolute structure S_o (*vs.* I_o) are as follows[90]:

i) A coordinate set $+x_j$ is found by solving the structure, using f''=0.0. This set and its inverse, $-x_j$, are then used, with the same thermal isotropic parameters, scale factor and +f'', to calculate F_c's for both structures without any further L.S. refinement. This obtains two different residuals, R^+ and R^-. Hamilton's test is then applied to determine the significance of the R-ratio.

ii) A coordinate set $+x_j$ is found by solving the structure, using f''=0.0. This set is then used to calculate F_c's for two structures (without further refinement), one with +f'', one with -f'', giving two residuals, R^+ and R^-.

¶ S_o *represents the correct absolute structure*
I_o *represents the inverse structure of* S_o

Hamilton's test is then used to determine the significance of this R-ratio.

The advantage of the latter method is that all coordinates and the space-group are kept intact, and only the sign of f'' for all atom types needs to be changed. It is thus especially useful with the nine anomolous pairs of space-groups.

Delaying evaluation of the R-ratio until after a few cycles of refinement with complex scattering factors enhances the ratio. However, Rogers[96] pointed out that a comparison using Hamilton's test on such an R-ratio is not valid, because the dimension of the hypothesis made becomes ill-defined.

c) Inverting a Structure S_o to I_o

For every non-centosymmetric structure S_o there exists a second structure I_o, which is the inverse of S_o - it has the same unit cell and origin as S_o.

This, however, is not true for the eleven enantiomorphic pairs of space-groups. Inverting the structure requires a change to the related space-group (see Table A-2).

In all other cases, it is possible in principle to superimpose S_o and I_o to yield a centrosymmetric structure, any of whose centers of symmetry, C, constitute an inversion center between S_o and I_o. In all but nine cases C coincides with the origin. In the nine anomalous space-groups (see Table A-3), the preferred origins O of the S_o and I_o structures do not coincide with the center-of-symmetry in the S+I structure. In these cases inversion is not straight-

forward.

$P4_1$	$P4_3$
$P4_122$	$P4_322$
$P4_12_12$	$P4_32_12$
$P3_1$	$P3_2$
$P3_112$	$P3_212$
$P3_121$	$P3_221$
$P6_1$	$P6_5$
$P6_2$	$P6_4$
$P6_122$	$P6_522$
$P6_222$	$P6_422$
$P4_132$	$P4_332$

Table A-2 The eleven enantiomporphic pairs of space-groups

Fdd2	$I4_1$
$F4_132$	$I4_122$
$P42_12$	$I4_1md$
$P\bar{4}2c$	$I\bar{4}2d$
	$I4_1cd$

Table A-3 The nine abnormal space-groups

d) Tests to Distinguish S_o from I_o

i) Hamilton's Test[85]

The ratio of the two residuals R^+ and R^- (as obtained in (c) above), R, is compared with a statistical $R_{b,N,\alpha}$, where

b = dimension of the hypothesis that the structure with higher residual is the absolute structure

N = degrees of freedom, i.e. N - NP

α = significance level of the hypothesis

If the observed R ratio is smaller than the statistical R, the hypothesis that the structure with the higher residual is the correct one can be discarded at a significance level α.

Rogers[96] has pointed out that, if the structure refinement is based on a unique set of data (i.e. no Bijvoet pairs collected) and real scattering factors are used in the refinement prior to making the test, the set of coordinates $+x_j$ will be biased slightly towards the $|F_o|$'s in the particular set of data collected. If, however, Bijvoet pairs are recorded and averaged until the calculation of F_o's for $+x_j$ and $-x_j$, this bias is reduced.

ii) Rogers' η[96]:

A new least-squares variable η is introduced into every dispersion term: $i\eta f_j''$. η should refine to +1 or -1. The use of η, however, has shown some disadvantages:

1) the wrong chirality or absolute structure may be obtained, depending on the starting value of η;
2) η will have a finite error estimate when an infinite estimate is desired[97].

iii) Flack's x[97]:

In this method a least-squares parameter x is introduced in the structure factor calculation, such that

$$|F_c(h,x)|^2 = (1-x)|F_c(h)|^2 + x|F_c(-h)|^2$$

This parameter is refined together with all other least-squares parameters and gives an enantiomorph-polarity estimation with estimated standard deviation, without having the shortcomings of Rogers' η.

A P P E N D I X 2

APPLICATION OF GROUP FACTOR ANALYSIS TO SELECTED STRETCHING BANDS OF THE NICKEL COMPLEX

APPENDIX 2

APPLICATION OF GROUP FACTOR ANALYSIS TO SELECTED STRETCHING BANDS OF THE NICKEL COMPLEX

The symmetry of molecular structures makes it possible to apply the mathematics of groups to work out molecular problems[58]. The following rules apply:

(a) An appropriate basis is used to generate a reducible representation of the point group of the molecule.

(b) This representation is reduced to its constituent irreducible representations.

(c) The results are interpreted.

The number and symmetries of stretching and bending modes and their Raman/ir activities are determined by a vibrational analysis of the molecule.

For an N-atom molecule, each atom is assigned unit displacement vectors in the three Cartesian directions. On performing the symmetry operations of the molecular point group, the new vector positions are related to the old ones by $3N \times 3N$ matrices, the characters of which may be used as a reducible representation of the point group.The symmetry species of all molecular motions are then determined by expressing the reducible representation in terms of its constituent irreducible representations. The characters of the irreducible representations and their symmetries are listed in character tables, which also indicate which of the irreducible representations transform under the symmetry operations as Cartesian coordinates, x, y, z, as their squares and binary products, x^2, y^2, z^2, xy, xz, and yz, and as rotation vectors R_x, R_y and R_z.

The irreducible representations responsible for vibrations are then derived by removal of those relating to translation and rotation.

The infrared and Raman activities of vibrational modes may then be read directly from the relevant character table: a fundamental will be ir active if the normal mode which is excited belongs to the same representation as any one or several of the Cartesian coordinates, while it will be Raman active if the normal mode belongs to the same representation as squares and binary products of the Cartesian coordinates.

By using internal displacement vectors instead of unit Cartesian displacement vectors as a basis to generate a reducible representation of the point group, information about the vibrations in terms of stretching or bending of the bonds may be obtained.

In the following analyses, the symmetries of the complexes are those from the respective x-ray crystal structures. For the *cis*-complexes in the host structures the point symmetry is C_2, while the *trans*-complex in the sec-butylbenzene clathrate has D_{2h} for its point symmetry. The character tables for these two point groups are shown in Fig. A-2. Figures showing the bases for the reducible representations for the Ni-NCS, Ni-N(R) and NC-S stretching modes appear in Fig. A-3.

i) The Ni-NCS stretching mode in the C_2 *cis* complex:

The total number of reducible representations

$\Gamma_{Tot} = 2E + 0C_2$

This corresponds to the following irreducible representations:

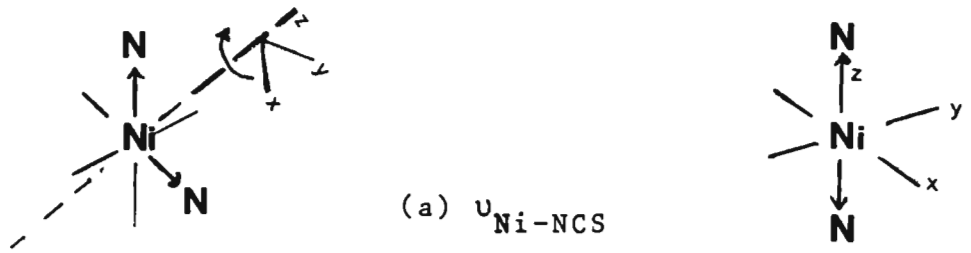
C_2	E	C_2		
A	1	1	z, R_z	x^2, y^2, z^2, xy
B	1	−1	x, y, R_x, R_y	yz, xz

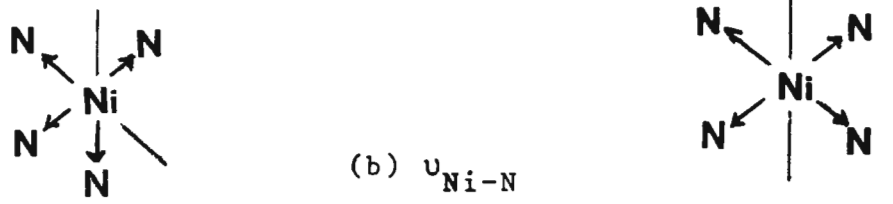
(a) Point group C_2

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

(b) Point group D_{2h}

Figure A-2 Character Tables





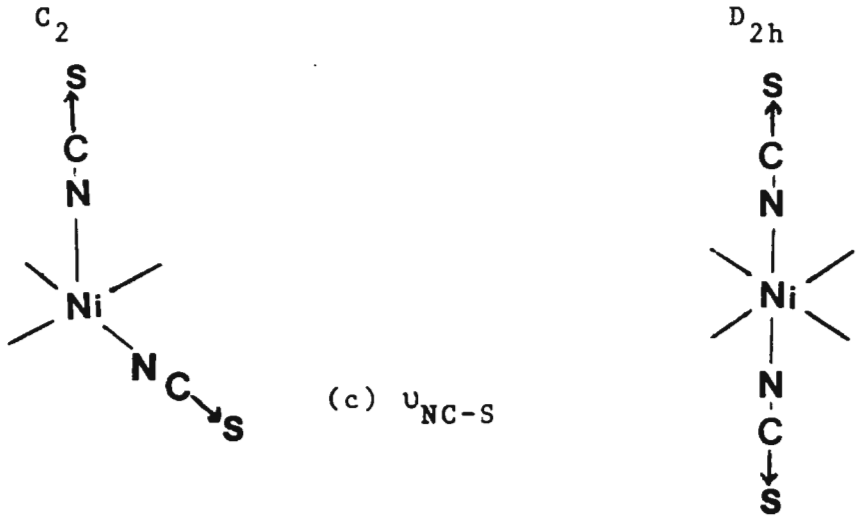


Figure A-3 Internal displacement vectors forming the bases for the reducible representations of some stretching modes.

$1/2(2A + 2B)$, and therefore

$\Gamma_{\upsilon Ni\text{-}NCS} = A + B$ (both modes are ir active)

ii) The Ni-NCS stretching mode in the D_{2h} *trans* complex:

$\Gamma_{Tot} = 2E + 2C_2(z) + 2\sigma(xz) + 2\sigma(yz)$

$\Gamma_{\upsilon Ni\text{-}NCS} = 1/8(8A_g + 8B_{1u}) = A_g + B_{1u}$

The A_g mode, however, is Raman active, leaving as ir active mode

$\Gamma_{\upsilon Ni\text{-}NCS} = B_{1u}$

iii) The Ni-N (amine) stretching modes in the C_2 *cis* complex:

$\Gamma_{Tot} = 4E + 0C_2$

$\Gamma_{\upsilon Ni\text{-}N} = 1/2(4A + 4B) = 2A + 2B$

iv) The Ni-N (amine) stretching modes in the D_{2h} *trans* complex:

$\Gamma_{Tot} = 4E + 2C_2(y) + 2C_2(x) + 4\sigma(xy) + 2\sigma(xz) + 2\sigma(yz)$

$\Gamma_{\upsilon Ni\text{-}N} = 1/8(16A_g + 8B_{2u} + 8B_{3u}) = 2A_g + B_{2u} + B_{3u}$

The A_g mode, however, is Raman active, leaving as ir active modes

$\Gamma_{\upsilon Ni\text{-}N} = B_{2u} + B_{3u}$

v) The NC-S stretching modes in the C_2 *cis* complex:

Two internal displacement vectors are related by the same symmetry as those in (i) above, giving rise to the same ir active modes:

$\Gamma_{\upsilon NC\text{-}S} = A + B$

vi) The NC-S stretching modes in the D_{2h} *trans* complex:

Two internal displacement vectors are related by the same symmetry as those in (ii) above, giving rise to the same ir active mode:

$\Gamma_{\upsilon NC\text{-}S} = B_{1u}$

A P P E N D I X 3

CONSTRUCTION OF AN ORGEL DIAGRAM FOR Ni(II)

APPENDIX 3

CONSTRUCTION OF AN ORGEL DIAGRAM FOR Ni(II)

The variation in energies of the various energy levels with increasing ligand field strength has been calculated by Orgel for the weak-field case, and diagrams relating the relative energy terms to the magnitude of D_q are called Orgel diagrams.

The spin-allowed transitions for Ni(II) (d^8) in an octahedral field result from transitions between levels derived from ^3F and ^3P. Three transitions are expected from the ground term:

$$^3A_{2g} \rightarrow {}^3T_{2g}; \quad {}^3A_{2g} \rightarrow {}^3T_{1g}(F); \quad {}^3A_{2g} \rightarrow {}^3T_{1g}(P)$$

Values for these transitions of some octahedral nickel(II) complexes appear in Table A-4, from which the Orgel diagram in Fig.A-4 was constructed. (Note: $E(^3A_{2g}) = -12D_q$ [98])

From the diagram constructed specifically for Ni^{2+}, the expected position of the $^3A_{1g} \rightarrow {}^3T_{2g}$ transition can be deduced for the complex for which only the two other transitions are known. To do this the vertical line which corresponds to $^3A_{2g} \rightarrow {}^3T_{1g}(F) = 15528cm^{-1}$ (≡ 644nm) has to be found. An approximate value of the energy of the $^3A_{1g} \rightarrow {}^3T_{2g}$ transition can then be determined. For $[Ni(NCS)_2(\alpha\text{-phenylethylamine})_4]$ it is found to be $\simeq 9300cm^{-1}$ (≡ 10750nm).

Complex	$^3A_{2g} \rightarrow {}^3T_{2g}$	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
$NiBr_2$	6800	11800	20600
$NiCl_2$	7200	11500	21900
$KNiF_3$	7250	12530	23810
$[Ni(DMSO)_6]^{2+}$	7728	12970	24038
$[Ni(MeOH)_6]^{2+}$	8430	14226	25000
$[Ni(H_2O)_6]^{2+}$	8500	13800	25300
$[Ni(etu)_6]^{2+}$	8000	13500	19100
$[Ni(NCS)_6]^{4-}$	9600	15950	25800
$[Ni(MeNH_2)_6]^{2+}$	10000	16779	27322
$[Ni(NH_3)_6]^{2+}$	10750	17500	28200
$[Ni(MeCN)_6]^{2+}$	10700	17400	27810
$[Ni(en)_3]^{2+}$	11200	18350	29000
$[Ni(dipy)_3]^{2+}$	12650	19200	—
$[Ni(phen)_3]^{2+}$	12700	19300	—

Table A-4 Electronic Spectra (cm^{-1}) of some Octahedral Nickel(II) Complexes [98]

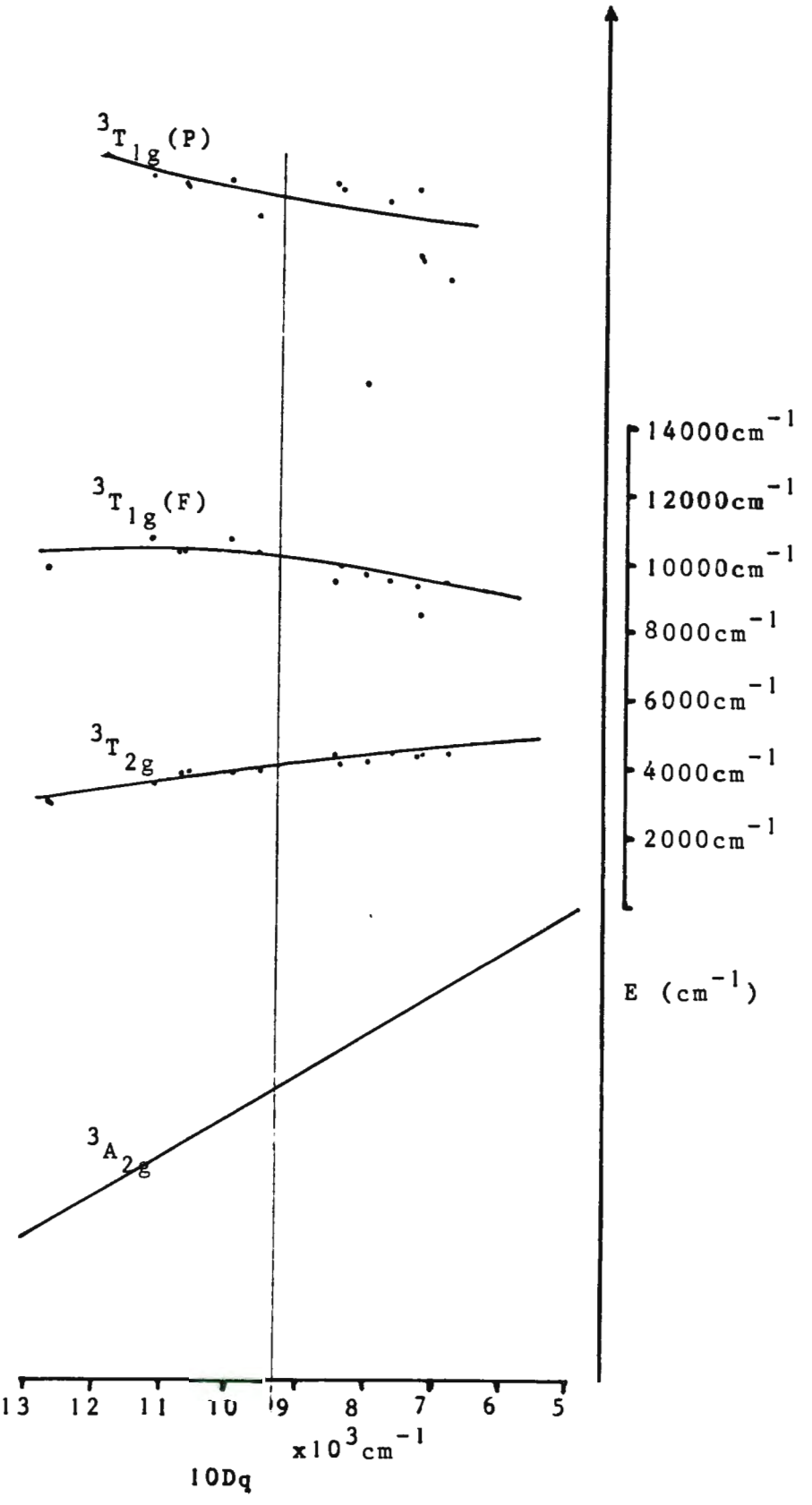


Figure A-4 Orgel Diagram for Ni(II)

APPENDIX 4

FRACTIONAL ATOMIC COORDINATES OF THE ATOMS LOCATED IN THE BEST MODEL OBTAINED OF THE *O*-XYLENE CLATHRATE

FRACTIONAL ATOMIC COORDINATES OF THE ATOMS LOCATED IN THE BEST MODEL OBTAINED OF THE *O*-XYLENE CLATHRATE

Atom	*x/a*	*y/b*	*z/c*
Ni1	.2464	.1068	.0231
N11	.2504	-.0114	-.0277
C11	.2430	-.0688	-.0653
S11	.2604	.3534	-.1200
N12	.2439	.2247	.0735
C12	.2443	.2843	.1093
S12	.2550	.3627	.1651
N13	.2969	.1679	-.0433
C131	.3145	.1042	-.1160
C132	.3035	.1435	-.1710
C133	.3711	.1659	-.1141
C134	.3670	.2264	-.1443
C135	.4127	.2804	-.1705
C136	.4495	.2262	-.1576
C137	.4567	.1706	-.1187
C138	.4112	.1306	-.1054
N14	.1923	.1572	-.0463
C141	.1722	.1183	-.0986
C142	.1344	.1287	-.1496
C143	.1471	.0825	-.0709
C144	.1129	.1245	-.0363
C145	.0492	.0976	.0067
C146	.0870	.0939	.0011
C147	.0823	.0016	-.0173
C148	.1334	-.0044	-.0659

Atom	*x/a*	*y/b*	*z/c*
N15	.1985	.0588	.0844
C151	.1802	.1057	.1409
C152	.2018	.1097	.2044
C153	.1325	.0787	.1608
C154	.0989	.1168	.1731
C155	.0560	.0880	.2030
C156	.0493	-.0109	.2274
C157	.0908	-.0556	.2098
C158	.1325	-.0089	.1857
N16	.2974	.0436	.0958
C161	.3294	.0900	.1547
C162	.3303	.0370	.2129
C163	.3679	.1356	.1152
C164	.3681	.2200	.1199
C165	.4060	.2585	.0904
C166	.4354	.2103	.0776
C167	.4356	.1278	.0852
C168	.4019	.0766	.1003
C1G	.3584	.1525	.5561
C2G	.3500	.1161	.4734
C3G	.3896	.0987	.4458
C4G	.4323	.1180	.4748
C5G	.4351	.1454	.5428
C6G	.3946	.1519	.5952

A P P E N D I X 5

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR THE 1:1 [Ni(NCS)$_2$*RRRR*]:[Ni(NCS)$_2$*RRSS*] COMPLEX

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PEROVSKITE STRUCTURE

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	0	0	54	61	12	2	0	24	24	2	5	0	23	23	11	7	0	44	45	1	11	0	61	60
4	0	0	67	67	13	2	0	11	6	3	5	0	93	92	13	7	0	39	36	2	11	0	22	25
6	0	0	49	53	14	2	0	32	31	4	5	0	54	57	0	8	0	79	80	3	11	0	66	67
8	0	0	68	70	16	2	0	19	19	5	5	0	100	99	1	8	0	79	79	5	11	0	33	33
10	0	0	15	14	18	2	0	15	16	6	5	0	17	15	2	8	0	56	55	7	11	0	31	29
12	0	0	39	38	1	3	0	33	31	7	5	0	57	61	3	8	0	24	27	8	11	0	17	12
14	0	0	36	36	2	3	0	26	28	8	5	0	24	25	4	8	0	69	64	9	11	0	30	31
16	0	0	27	25	3	3	0	282	281	9	5	0	53	55	5	8	0	32	30	11	11	0	22	22
1	1	0	217	211	4	3	0	62	59	10	5	0	13	17	6	8	0	66	65	13	11	0	22	18
2	1	0	15	13	5	3	0	99	98	11	5	0	50	50	7	8	0	15	9	14	11	0	12	6
3	1	0	81	78	6	3	0	24	24	13	5	0	27	25	8	8	0	52	54	0	12	0	56	55
4	1	0	35	32	7	3	0	30	30	15	5	0	25	27	9	8	0	11	17	1	12	0	19	18
5	1	0	13	16	8	3	0	12	12	17	5	0	19	17	10	8	0	35	33	2	12	0	56	59
6	1	0	48	47	9	3	0	43	47	0	6	0	69	71	12	8	0	46	45	3	12	0	21	21
7	1	0	69	75	10	3	0	22	25	1	6	0	38	33	14	8	0	21	19	4	12	0	35	35
8	1	0	51	47	11	3	0	47	48	2	6	0	32	34	1	9	0	74	77	5	12	0	19	20
9	1	0	34	35	13	3	0	27	24	3	6	0	20	21	2	9	0	21	22	6	12	0	15	17
10	1	0	10	9	15	3	0	29	28	4	6	0	72	71	3	9	0	15	12	8	12	0	26	23
11	1	0	40	38	17	3	0	20	20	6	6	0	81	87	4	9	0	10	8	10	12	0	25	27
12	1	0	17	15	0	4	0	178	177	7	6	0	15	14	5	9	0	51	52	12	12	0	14	13
13	1	0	38	39	1	4	0	65	65	8	6	0	63	64	7	9	0	54	54	1	13	0	42	40
15	1	0	22	24	2	4	0	139	140	10	6	0	63	61	8	9	0	17	21	2	13	0	35	35
17	1	0	14	19	4	4	0	119	123	11	6	0	20	18	9	9	0	29	33	3	13	0	38	43
0	2	0	183	181	5	4	0	41	39	12	6	0	29	30	11	9	0	30	31	5	13	0	23	22
1	2	0	18	19	6	4	0	42	46	16	6	0	14	16	13	9	0	19	20	6	13	0	11	9
2	2	0	27	26	7	4	0	25	25	1	7	0	22	23	0	10	0	45	48	9	13	0	14	13
3	2	0	73	76	8	4	0	58	56	2	7	0	30	29	2	10	0	41	45	0	14	0	36	36
4	2	0	70	67	9	4	0	24	24	3	7	0	16	16	4	10	0	47	45	2	14	0	26	27
5	2	0	29	30	10	4	0	74	75	4	7	0	22	24	6	10	0	31	31	3	14	0	13	13
6	2	0	72	73	12	4	0	28	30	5	7	0	83	82	8	10	0	32	31	4	14	0	30	32
7	2	0	8	5	14	4	0	39	39	6	7	0	11	10	9	10	0	23	22	6	14	0	21	21
8	2	0	82	83	16	4	0	31	29	7	7	0	104	103	10	10	0	34	33	8	14	0	15	17
10	2	0	22	23	18	4	0	22	19	8	7	0	9	15	12	10	0	18	22	1	15	0	18	19
11	2	0	13	13	1	5	0	10	9	9	7	0	41	43	14	10	0	13	15	3	15	0	30	27
5	15	0	33	31	-12	2	1	15	18	1	3	1	12	15	9	4	1	19	19	-4	6	1	12	11
4	16	0	27	24	-9	2	1	14	17	2	3	1	51	47	-12	5	1	11	11	-3	6	1	15	13
3	17	0	20	18	-8	2	1	37	37	3	3	1	110	109	-11	5	1	18	18	-2	6	1	16	17
0	18	0	22	19	-7	2	1	31	31	4	3	1	41	38	-10	5	1	17	21	-1	6	1	39	39
0	0	1	16	15	-6	2	1	103	100	5	3	1	32	27	-8	5	1	17	19	0	6	1	11	16
1	0	1	31	30	-5	2	1	34	34	6	3	1	31	31	-7	5	1	35	31	1	6	1	44	40
2	0	1	51	50	-4	2	1	44	46	7	3	1	28	31	-6	5	1	39	37	2	6	1	18	17
3	0	1	61	62	-3	2	1	66	68	8	3	1	15	15	-5	5	1	38	35	3	6	1	12	13
4	0	1	55	55	-2	2	1	63	60	9	3	1	11	9	-4	5	1	59	60	4	6	1	9	12
8	0	1	31	29	-1	2	1	62	63	10	3	1	14	13	-3	5	1	51	46	5	6	1	34	33
9	0	1	23	24	0	2	1	10	8	11	3	1	14	13	-2	5	1	40	37	6	6	1	39	41
12	0	1	17	16	1	2	1	60	64	12	3	1	11	9	-1	5	1	41	43	7	6	1	24	25
-11	1	1	31	29	2	2	1	62	61	14	3	1	11	9	0	5	1	12	13	8	6	1	25	25
-9	1	1	32	33	3	2	1	63	67	-14	4	1	14	8	1	5	1	43	42	9	6	1	14	9
-8	1	1	29	27	4	2	1	48	46	-12	4	1	12	13	2	5	1	37	37	10	6	1	25	23
-7	1	1	37	34	5	2	1	32	33	-11	4	1	10	6	3	5	1	47	46	11	6	1	20	19
-6	1	1	47	45	6	2	1	94	100	-9	4	1	18	18	4	5	1	57	60	12	6	1	21	20
-5	1	1	61	56	7	2	1	30	31	-8	4	1	13	13	5	5	1	33	34	13	6	1	14	12
-4	1	1	90	87	8	2	1	37	37	-7	4	1	42	40	6	5	1	38	37	15	6	1	13	10
-3	1	1	20	21	11	2	1	13	12	-6	4	1	35	35	7	5	1	32	30	-10	7	1	19	19
-2	1	1	63	64	12	2	1	17	18	-5	4	1	59	59	8	5	1	17	18	-7	7	1	31	31
-1	1	1	21	23	-12	3	1	13	9	-4	4	1	35	33	10	5	1	20	21	-6	7	1	12	9
0	1	1	28	26	-11	3	1	14	14	-3	4	1	62	68	11	5	1	20	18	-5	7	1	43	43
1	1	1	21	23	-10	3	1	16	14	-2	4	1	94	102	13	5	1	13	14	-4	7	1	22	20
2	1	1	60	63	-9	3	1	11	8	-1	4	1	41	39	14	5	1	14	14	-3	7	1	16	14
3	1	1	27	22	-8	3	1	14	15	0	4	1	78	75	15	5	1	11	10	-1	7	1	27	27
4	1	1	84	86	-7	3	1	32	31	1	4	1	38	39	-13	6	1	14	13	0	7	1	29	29
5	1	1	57	55	-6	3	1	32	31	2	4	1	107	103	-12	6	1	20	20	1	7	1	28	27
6	1	1	46	45	-5	3	1	29	27	3	4	1	65	67	-11	6	1	21	19	2	7	1	9	12
7	1	1	32	34	-4	3	1	43	38	4	4	1	28	33	-10	6	1	25	23	3	7	1	17	14
8	1	1	31	27	-3	3	1	108	109	5	4	1	59	59	-9	6	1	24	26	4	7	1	21	20
9	1	1	30	33	-2	3	1	48	48	6	4	1	38	35	-7	6	1	27	26	5	7	1	45	44
11	1	1	31	29	-1	3	1	11	15	7	4	1	39	40	-6	6	1	41	41	7	7	1	31	31
12	1	1	13	10	0	3	1	103	102	8	4	1	11	13	-5	6	1	32	33	10	7	1	19	19

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PELDAR STRUCTURE

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
12	7	1	15	13	-9	10	1	13	7	3	14	1	16	12	0	1	2	187	189	4	2	2	66	73
-12	9	1	15	14	-7	10	1	22	19	7	14	1	17	14	1	1	2	48	47	5	2	2	87	83
-10	8	1	20	19	-5	10	1	23	26	10	14	1	11	4	2	1	2	27	29	6	2	2	27	27
-9	8	1	13	15	-3	10	1	40	41	0	15	1	11	4	3	1	2	67	72	7	2	2	61	69
-8	8	1	13	13	-2	10	1	22	22	6	15	1	12	10	4	1	2	103	107	8	2	2	38	40
-7	6	1	21	22	2	10	1	21	22	0	0	2	105	102	5	1	2	19	18	9	2	2	48	49
-6	8	1	28	28	3	10	1	43	42	1	0	2	151	151	6	1	2	48	51	10	2	2	29	32
-5	8	1	19	19	5	10	1	23	26	2	0	2	37	33	7	1	2	41	41	11	2	2	37	39
-4	9	1	17	15	7	10	1	20	19	3	0	2	224	226	8	1	2	60	62	12	2	2	37	35
-3	8	1	31	30	8	10	1	12	11	4	0	2	84	84	10	1	2	47	47	13	2	2	21	22
-2	9	1	33	33	10	10	1	22	20	5	0	2	61	58	11	1	2	35	34	14	2	2	23	25
-1	8	1	22	21	11	10	1	12	11	6	0	2	31	30	12	1	2	34	33	15	2	2	19	20
0	8	1	20	20	-9	11	1	11	9	8	0	2	22	21	13	1	2	22	21	-14	3	2	37	36
1	8	1	20	21	-6	11	1	18	17	9	0	2	58	60	14	1	2	14	15	-13	3	2	20	18
2	8	1	35	33	-4	11	1	16	14	10	0	2	27	25	15	1	2	15	15	-12	3	2	30	28
3	8	1	29	30	-2	11	1	30	27	11	0	2	42	41	16	1	2	24	24	-11	3	2	28	27
4	8	1	19	15	-1	11	1	17	16	12	0	2	29	27	-14	2	2	21	23	-10	3	2	29	17
5	8	1	19	19	0	11	1	24	21	13	0	2	11	11	-13	2	2	26	23	-9	3	2	25	27
6	8	1	30	28	1	11	1	18	16	15	0	2	24	23	-12	2	2	36	33	-8	3	2	71	67
7	8	1	20	22	2	11	1	30	28	16	0	2	14	12	-11	2	2	37	37	-7	3	2	48	49
8	8	1	13	13	3	11	1	18	16	17	0	2	25	23	-10	2	2	33	34	-6	3	2	97	98
10	8	1	18	19	4	11	1	12	14	-13	1	2	20	20	-9	2	2	53	49	-5	3	2	48	52
12	8	1	15	14	6	11	1	12	17	-12	1	2	35	33	-8	2	2	41	41	-4	3	2	52	58
-11	9	1	15	13	-8	12	1	18	14	-11	1	2	33	34	-7	2	2	73	72	-3	3	2	13	14
-7	9	1	23	23	-4	12	1	14	13	-10	1	2	45	46	-6	2	2	24	25	-2	3	2	144	144
-6	9	1	12	13	-2	12	1	16	15	-9	1	2	11	12	-5	2	2	84	84	-1	3	2	138	140
-4	9	1	34	35	4	12	1	17	13	-8	1	2	62	62	-4	2	2	68	73	0	3	2	95	92
-3	9	1	11	12	8	12	1	17	14	-7	1	2	38	40	-3	2	2	93	87	1	3	2	142	143
4	9	1	36	35	9	12	1	13	9	-6	1	2	54	53	-2	2	2	90	86	2	3	2	142	140
6	9	1	12	13	-6	13	1	15	11	-5	1	2	14	15	-1	2	2	79	78	3	3	2	12	13
7	9	1	25	23	1	13	1	11	5	-4	1	2	102	101	0	2	2	77	76	4	3	2	58	55
11	9	1	18	13	-1	14	1	12	13	-3	1	2	79	75	1	2	2	84	85	5	3	2	51	55
12	9	1	12	12	0	14	1	12	12	-2	1	2	40	35	2	2	2	87	84	6	3	2	93	97
-10	10	1	22	20	1	14	1	12	12	-1	1	2	46	45	3	2	2	86	86	7	3	2	49	49
8	3	2	63	68	13	4	2	42	42	-9	6	2	38	39	-1	7	2	26	24	7	8	2	32	33
9	3	2	21	25	14	4	2	21	19	-8	6	2	35	37	0	7	2	50	50	8	8	2	20	22
10	3	2	20	21	15	4	2	27	27	-7	6	2	56	55	1	7	2	22	21	9	8	2	36	34
11	3	2	27	27	-12	5	2	17	22	-6	6	2	47	49	2	7	2	45	43	11	8	2	33	35
12	3	2	27	28	-10	5	2	42	43	-5	6	2	54	52	3	7	2	66	64	12	8	2	28	25
13	3	2	21	20	-9	5	2	35	35	-4	6	2	70	68	4	7	2	72	70	13	8	2	21	21
14	3	2	33	35	-8	5	2	60	60	-3	6	2	48	46	5	7	2	25	22	15	8	2	13	14
15	3	2	16	13	-7	5	2	50	51	-2	6	2	41	40	6	7	2	28	24	-11	9	2	31	28
-14	4	2	22	18	-6	5	2	57	56	-1	6	2	56	61	7	7	2	19	18	-10	9	2	30	27
-13	4	2	47	44	-5	5	2	58	59	0	6	2	30	30	8	7	2	39	41	-9	9	2	25	27
-11	4	2	32	32	-4	5	2	25	20	1	6	2	59	62	9	7	2	26	27	-8	9	2	18	18
-10	4	2	17	19	-3	5	2	53	54	2	6	2	36	38	10	7	2	58	59	-7	9	2	33	33
-9	4	2	34	34	-2	5	2	88	85	3	6	2	49	49	12	7	2	24	25	-6	9	2	36	38
-8	4	2	32	33	-1	5	2	65	65	4	6	2	71	68	13	7	2	21	21	-5	9	2	24	26
-7	4	2	74	78	0	5	2	108	106	5	6	2	48	49	14	7	2	12	16	-4	9	2	67	68
-6	4	2	68	65	1	5	2	62	63	6	6	2	50	49	16	7	2	15	15	-2	9	2	37	39
-5	4	2	57	61	2	5	2	85	86	7	6	2	56	55	-12	8	2	29	26	-1	9	2	28	29
-4	4	2	34	33	3	5	2	51	52	8	6	2	37	37	-11	8	2	36	35	0	9	2	22	22
-3	4	2	24	20	4	5	2	20	24	9	6	2	39	39	-9	8	2	39	37	1	9	2	30	29
-2	4	2	81	79	5	5	2	58	58	10	6	2	24	28	-8	8	2	21	21	2	9	2	41	41
-1	4	2	130	130	6	5	2	55	54	11	6	2	33	34	-7	8	2	37	32	3	9	2	15	14
0	4	2	33	29	7	5	2	45	50	13	6	2	24	23	-6	8	2	24	24	4	9	2	68	69
1	4	2	141	135	8	5	2	59	60	14	6	2	20	16	-5	8	2	55	57	5	9	2	23	26
2	4	2	77	75	9	5	2	34	35	-12	7	2	25	25	-4	8	2	47	46	6	9	2	37	39
3	4	2	9	16	10	5	2	42	42	-11	7	2	21	18	-3	8	2	66	72	7	9	2	32	34
4	4	2	35	36	11	5	2	17	17	-10	7	2	58	59	-2	8	2	47	51	8	9	2	16	17
5	4	2	53	59	12	5	2	19	21	-9	7	2	25	26	-1	8	2	56	53	9	9	2	25	27
6	4	2	65	66	14	5	2	27	26	-8	7	2	41	41	0	8	2	20	20	10	9	2	29	26
7	4	2	76	80	15	5	2	20	17	-7	7	2	22	20	1	8	2	54	52	11	9	2	29	27
8	4	2	33	33	16	5	2	17	13	-6	7	2	26	23	2	8	2	54	54	12	9	2	20	21
9	4	2	34	36	-13	6	2	24	23	-5	7	2	24	22	3	8	2	73	72	14	9	2	15	15
10	4	2	18	18	-12	6	2	11	12	-4	7	2	69	67	4	8	2	45	44	-10	10	2	21	21
11	4	2	31	32	-11	6	2	32	34	-3	7	2	64	63	5	8	2	57	58	-7	10	2	34	34
12	4	2	13	11	-10	6	2	26	28	-2	7	2	49	47	6	8	2	23	24	-6	10	2	19	21

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PELDAA STRUCTURE

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	10	2	41	44	1	12	2	29	28	3	16	2	12	11	6	2	3	22	23	1	6	3	64	63
-4	10	2	17	17	2	12	2	18	18	0	17	2	19	18	7	2	3	19	22	2	6	3	30	29
-3	10	2	50	53	3	12	2	36	36	5	17	2	17	13	8	2	3	27	27	3	6	3	18	20
-2	10	2	25	25	4	12	2	25	23	0	18	2	14	11	9	2	3	27	29	4	6	3	22	25
-1	10	2	20	20	5	12	2	33	32	0	0	3	71	70	11	2	3	14	15	5	6	3	29	30
0	10	2	49	47	6	12	2	12	16	1	0	3	30	32	0	3	3	94	93	6	6	3	16	17
1	10	2	16	18	7	12	2	23	24	2	0	3	12	14	1	3	3	37	40	7	6	3	31	26
2	10	2	26	26	8	12	2	13	13	3	0	3	69	70	2	3	3	65	68	8	6	3	12	12
3	10	2	53	52	9	12	2	23	20	4	0	3	17	20	3	3	3	39	40	9	6	3	25	29
4	10	2	15	14	10	12	2	18	17	5	0	3	19	16	4	3	3	59	57	10	6	3	28	32
5	10	2	42	46	11	12	2	18	16	6	0	3	34	32	5	3	3	62	64	11	6	3	18	14
6	10	2	19	21	13	12	2	16	15	7	0	3	44	41	6	3	3	40	37	12	6	3	17	16
7	10	2	34	34	0	13	2	32	30	8	0	3	13	15	7	3	3	59	60	0	7	3	33	33
8	10	2	10	6	2	13	2	29	30	9	0	3	21	21	8	3	3	18	19	1	7	3	17	17
10	10	2	21	21	3	13	2	27	27	10	0	3	26	27	0	4	3	42	39	2	7	3	47	47
11	10	2	24	23	4	13	2	22	21	11	0	3	22	19	1	4	3	55	53	3	7	3	50	47
12	10	2	20	23	5	13	2	17	16	0	1	3	39	40	2	4	3	89	82	4	7	3	39	39
13	10	2	19	20	6	13	2	19	17	1	1	3	105	106	3	4	3	20	18	5	7	3	23	23
-6	11	2	40	43	8	13	2	22	21	2	1	3	117	120	4	4	3	33	35	7	7	3	24	26
-4	11	2	46	47	0	14	2	16	15	3	1	3	46	46	5	4	3	37	32	8	7	3	25	20
-3	11	2	23	23	1	14	2	28	31	4	1	3	73	79	7	4	3	21	17	11	7	3	13	13
-2	11	2	45	43	2	14	2	18	19	5	1	3	12	9	8	4	3	16	13	1	8	3	34	33
-1	11	2	31	29	4	14	2	19	21	6	1	3	38	42	9	4	3	15	12	2	8	3	36	35
0	11	2	27	28	5	14	2	18	19	7	1	3	10	11	14	4	3	11	8	3	8	3	21	17
1	11	2	28	28	7	14	2	18	13	8	1	3	10	14	0	5	3	58	57	4	8	3	22	21
2	11	2	47	45	9	14	2	17	19	9	1	3	37	35	2	5	3	64	61	8	8	3	25	23
3	11	2	25	23	10	14	2	13	11	11	1	3	11	14	3	5	3	28	31	10	8	3	22	17
4	11	2	50	45	0	15	2	26	26	13	1	3	11	11	4	5	3	46	43	1	9	3	27	29
6	11	2	36	42	2	15	2	17	18	0	2	3	29	33	5	5	3	39	36	2	9	3	14	18
8	11	2	21	20	6	15	2	16	14	1	2	3	207	204	6	5	3	42	42	4	9	3	17	18
9	11	2	17	15	7	15	2	13	10	2	2	3	133	133	7	5	3	19	16	5	9	3	23	22
10	11	2	24	22	8	15	2	26	20	3	2	3	104	107	8	5	3	10	12	7	9	3	28	28
11	11	2	20	18	9	15	2	11	9	4	2	3	33	35	9	5	3	19	16	8	9	3	13	6
12	11	2	21	19	1	16	2	16	20	5	2	3	55	59	11	5	3	22	24	9	9	3	10	11
15	9	3	11	9	3	1	4	37	38	7	3	4	48	46	14	5	4	20	20	4	8	4	25	26
0	10	3	36	41	4	1	4	41	45	8	3	4	35	38	16	5	4	15	14	5	8	4	41	41
1	10	3	24	24	5	1	4	19	16	9	3	4	20	18	0	6	4	49	53	6	8	4	41	42
4	10	3	17	17	6	1	4	99	96	10	3	4	57	59	1	6	4	79	75	7	8	4	32	31
5	10	3	12	10	7	1	4	41	42	11	3	4	22	22	2	6	4	42	43	9	8	4	13	11
6	10	3	28	29	8	1	4	81	85	12	3	4	26	27	3	6	4	119	120	10	8	4	18	15
7	10	3	10	9	9	1	4	43	45	14	3	4	17	16	4	6	4	48	48	11	8	4	29	25
1	11	3	29	27	10	1	4	24	25	15	3	4	12	10	5	6	4	60	60	13	8	4	26	24
2	11	3	12	15	11	1	4	23	22	16	3	4	21	18	6	6	4	35	34	0	9	4	62	66
4	11	3	20	19	12	1	4	44	43	0	4	4	12	16	7	6	4	42	46	1	9	4	36	39
6	11	3	13	13	13	1	4	18	17	1	4	4	60	58	8	6	4	22	26	2	9	4	37	40
7	11	3	15	19	14	1	4	23	24	2	4	4	52	51	9	6	4	11	13	3	9	4	32	34
5	12	3	13	10	0	2	4	67	68	3	4	4	97	99	10	6	4	33	33	4	9	4	21	24
8	12	3	42	10	1	2	4	89	92	4	4	4	47	49	11	6	4	32	31	5	9	4	14	12
3	13	3	16	15	2	2	4	51	48	5	4	4	30	30	12	6	4	16	14	6	9	4	46	47
3	14	3	19	16	3	2	4	43	44	6	4	4	47	46	13	6	4	28	26	7	9	4	17	12
4	14	3	24	23	4	2	4	32	30	8	4	4	14	14	15	6	4	13	16	8	9	4	39	40
2	17	3	13	4	5	2	4	62	64	9	4	4	44	44	0	7	4	107	107	10	9	4	24	22
1	0	4	92	92	6	2	4	46	45	11	4	4	46	50	1	7	4	56	55	11	9	4	12	13
2	0	4	29	35	7	2	4	87	90	12	4	4	22	22	2	7	4	60	61	12	9	4	22	22
3	0	4	54	54	8	2	4	51	48	15	4	4	19	19	3	7	4	42	44	0	10	4	13	15
4	0	4	40	37	9	2	4	68	67	17	4	4	17	17	4	7	4	37	39	1	10	4	48	48
5	0	4	37	40	10	2	4	32	32	0	5	4	90	85	5	7	4	33	32	2	10	4	40	39
6	0	4	29	28	11	2	4	36	40	1	5	4	63	59	6	7	4	46	45	3	10	4	30	30
7	0	4	144	145	12	2	4	20	21	2	5	4	102	99	7	7	4	15	20	4	10	4	16	15
8	0	4	63	63	13	2	4	19	22	3	5	4	56	58	8	7	4	13	15	5	10	4	22	25
9	0	4	54	55	15	2	4	23	22	4	5	4	91	96	9	7	4	19	18	6	10	4	17	17
10	0	4	14	16	17	2	4	19	16	5	5	4	61	60	10	7	4	14	14	7	10	4	28	28
13	0	4	47	44	1	3	4	46	43	6	5	4	37	39	12	7	4	24	27	8	10	4	18	16
14	0	4	16	12	2	3	4	85	80	7	5	4	24	25	14	7	4	31	30	9	10	4	12	10
15	0	4	22	23	3	3	4	35	38	8	5	4	20	21	0	8	4	41	38	10	10	4	22	21
0	1	4	67	67	4	3	4	120	122	9	5	4	15	16	1	8	4	78	76	11	10	4	23	24
1	1	4	59	62	5	3	4	79	79	10	5	4	46	47	2	8	4	38	40	0	11	4	27	31
2	1	4	33	30	6	3	4	36	37	13	5	4	13	11	3	8	4	41	46	2	11	4	28	27

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PELDAA STRUCTURE

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
3	11	4	28	29	0	15	4	14	8	4	2	5	61	63	15	4	5	19	14	4	8	5	22	21
4	11	4	34	32	2	15	4	16	18	5	2	5	15	17	0	5	5	10	5	5	8	5	20	22
5	11	4	22	22	4	15	4	21	20	6	2	5	46	43	1	5	5	32	32	6	8	5	22	22
6	11	4	28	27	3	16	4	15	13	7	2	5	22	21	2	5	5	8	7	8	8	5	17	16
7	11	4	16	13	0	17	4	18	17	8	2	5	28	24	3	5	5	24	24	10	8	5	19	18
8	11	4	18	19	2	17	4	14	15	9	2	5	26	22	4	5	5	31	36	12	8	5	11	12
9	11	4	14	14	4	17	4	15	13	10	2	5	11	11	5	5	5	15	11	2	9	5	24	23
10	11	4	28	26	0	0	5	50	48	11	2	5	18	21	6	5	5	31	29	3	9	5	33	29
12	11	4	12	11	2	0	5	30	30	13	2	5	16	17	7	5	5	31	32	4	9	5	29	31
1	12	4	16	14	3	0	5	16	15	0	3	5	49	48	8	5	5	29	31	5	9	5	19	21
3	12	4	28	27	4	0	5	11	7	1	3	5	44	40	9	5	5	22	23	10	9	5	21	18
4	12	4	25	24	5	0	5	55	59	2	3	5	81	85	11	5	5	13	15	12	9	5	16	12
5	12	4	31	33	6	0	5	45	44	3	3	5	45	47	0	6	5	54	55	0	10	5	24	26
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PELDAA STRUCTURE

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	1	7	64	61	1	4	7	44	42	5	7	7	19	20	0	0	8	122	122	10	2	8	17	13
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PELDAA STRUCTURE

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7	11	11	15	12	2	5	12	11	14	4	1	13	23	24	6	5	13	20	17	7	5	14	11	10

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PELDAA STRUCTURE

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
9	6	14	12	9	1	1	15	16	19	3	3	15	15	11	4	6	15	21	22	0	5	16	15	7
0	7	14	14	12	5	1	15	21	16	5	3	15	17	17	1	7	15	19	16	2	5	16	13	12
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8	0	15	25	21																				

A P P E N D I X 6

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR THE 1:1 $[Ni(NCS)_2 RRSS]$:*SEC*-BUTYLBENZENE CLATHRATE

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PELDSBD STRUCTURE IN C2/C PAGE 1

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR THE $[Ni(NCS)_2 RRRR]$ STRUCTURE

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR MEDA FINAL FORM

PAGE 1

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PROA FINAL FORM

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PEOA FINAL FORM

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PEDA FINAL FORM

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-12	5	1	35	28																				

A P P E N D I X 8

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR THE $[Ni(NCS)_2SSSS]$ STRUCTURE IN TRICLINIC P1

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR PELB IN P1

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
1	-10	0	11	7	3	-6	0	20	22	-8	-3	0	20	19	-2	-1	0	39	38	5	1	0	30	29
0	-10	0	15	15	2	-6	0	25	26	-7	-3	0	13	13	-1	-1	0	90	86	6	1	0	17	14
-1	-10	0	14	14	1	-6	0	19	18	-6	-3	0	13	13	0	-1	0	117	103	7	1	0	26	23
-2	-10	0	12	11	0	-6	0	37	38	-5	-3	0	49	51	1	-1	0	88	86	8	1	0	28	27
-3	-10	0	6	7	-1	-6	0	44	45	-4	-3	0	16	19	2	-1	0	72	74	9	1	0	7	11
-5	-9	0	8	8	-2	-6	0	22	22	-3	-3	0	6	7	3	-1	0	84	85	10	1	0	10	9
-3	-9	0	8	6	-3	-6	0	15	18	-2	-3	0	8	10	4	-1	0	48	51	10	2	0	9	6
-2	-9	0	11	10	-4	-6	0	11	12	-1	-3	0	72	74	5	-1	0	50	49	9	2	0	11	12
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1	-9	0	9	9	-7	-6	0	17	16	2	-3	0	28	25	8	-1	0	29	31	6	2	0	24	25
2	-9	0	11	15	-8	-6	0	14	15	3	-3	0	11	12	9	-1	0	12	13	5	2	0	23	26
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7	-8	0	15	16	-6	-5	0	26	27	7	-3	0	19	19	8	0	0	33	33	1	2	0	77	78
6	-8	0	20	21	-5	-5	0	18	19	8	-3	0	16	15	7	0	0	42	42	0	2	0	33	32
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E FELSSTRUCTURE IN P1

R E F E R E N C E S

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