

Studies in Werner Clathrates. Part 2. Structures of  
bis(Isothiocyanato)tetra(4-phenylpyridine)nickel(II)·  
4-Dimethylsulphoxide,  
bis(Isothiocyanato)tetra(3-methylpyridine)nickel(II)·  
Chloroform and  
bis(Isothiocyanato)tetra(3,5-dimethylpyridine)nickel(II)

LUIGI R. NASSIMBENI\*, SEVI PAPANICOLAOU and MADELEINE H. MOORE  
*Department of Physical Chemistry, University of Cape Town, Rondebosch, 7700, South Africa*

(Received: 1 June 1984; revised 16 August 1985)

**Abstract.** The structures of  $\text{Ni}(\text{NCS})_2(4\text{-PhPy})_4 \cdot 4\text{DMSO}$  and  $\text{Ni}(\text{NCS})_2(3\text{-MePy})_4 \cdot \text{CHCl}_3$  have been elucidated. Movement of guest molecules through channels in the host structure was simulated by potential energy calculations.  $\text{Ni}(\text{NCS})_2(3,5\text{-diMePy})_4$  does not form inclusion compounds. An intra-molecular potential energy study shows that the *ortho*-hydrogens on the 3,5-dimethylpyridine ligands control the conformation of the molecule. The same result is obtained with the 4-methylpyridine ligand, which suggests that the extent of rotation of substituted pyridines about the Ni–N bonds is not a factor governing clathrate formation.

**Key words:** Werner clathrates, X-ray structure analyses, potential energy calculations, conformational studies.

**Supplementary Data** relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82030 (43 pages).

## 1. Introduction

Interest in coordination compounds as clathrating agents was stimulated by Schaeffer and Dorsey who announced a new way of separating mixtures of aromatic compounds [1]. These so-called Werner Clathrates comprise host molecules of general formula  $\text{MX}_2\text{L}_4$  ( $\text{M} = \text{Ni}, \text{Co}, \text{Fe}, \text{Mn}, \text{Zn}, \text{Cu}$ ;  $\text{X} = \text{SCN}, \text{CNO}, \text{NO}_2$ ;  $\text{L} =$  substituted pyridine or  $\alpha$ -alkylarylamine) and they entrap a variety of organic compounds as guest molecules. The most versatile complex thus far investigated has been  $\text{Ni}(\text{NCS})_2(4\text{-MePy})_4$ , and the structures and physico-chemical properties of its clathrates have been studied in several laboratories. The role of steric effects of intramolecular interactions of the host, and the intermolecular host-guest interactions have recently been reviewed by Lipkowski [2, 3]. Thermochemical studies of the clathration process have been carried out with  $\text{Ni}(\text{NCS})_2(4\text{-MePy})_4$  as host and xylene isomers as guests [4] and its selective properties as the stationary phase in chromatography have been studied [5].

We are extending the study of Werner clathrates by altering the host complex and analysing the host-guest interactions which occur upon clathration. Thus, we synthesised and characte-

\* Author for correspondence

riated  $\text{Ni}(\text{NCS})_2(4\text{-MePy})_2(4\text{-PhPy})_2 \cdot (2\text{-methoxyethanol})$  and  $\text{Ni}(\text{NCS})_2(4\text{-MePy})_4 \cdot p\text{-cymene}$ , and for the latter compound we estimated the host–guest association constant in solution using NMR spectroscopy [6]. In this contribution we report the structures of three new compounds and discuss molecular conformation and host–guest non-bonded energies.

## 2. Experimental and Structure Solution

### 2.1. $\text{Ni}(\text{NCS})_2(4\text{-PhPy})_4 \cdot 4\text{DMSO}$ , I

The host complex  $\text{Ni}(\text{NCS})_2(4\text{-PhPy})_4$ , prepared by the method of Schaeffer *et al.* [1], was dissolved in excess dimethyl sulphoxide and heated to the boiling temperature. Small purple-blue crystals of the clathrate appeared on slow cooling and were mounted in Lindemann capillary tubes with mother liquor to prevent deterioration in air. Preliminary cell dimensions and space group symmetry were determined photographically. Accurate cell constants were obtained from a least-squares analysis of the settings of 25 reflections measured on a Philips PW1100 four-circle diffractometer with graphite monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ).

During the diffractometer data collection, three reference reflections were periodically monitored to check crystal stability. Lorentz-polarization corrections were applied but no correction was made for absorption. Crystal data and experimental details of the data collection are listed in Table I. The structure was solved by the heavy-atom method using the SHELX-76 program system [7]. The four guest DMSO molecules appeared distinctly in the course of the refinement, although their final temperature factors were always higher than those of the host atoms.

Final refinement was carried out with the Ni and all S atoms treated anisotropically, and H atoms of the host molecule constrained at  $1.08 \text{ \AA}$  from their respective C atoms and with a common isotropic thermal parameter. Hydrogen atoms of the methyl groups of the DMSO guest molecules were not included in the final model.

The salient parameters from the final cycle of least-squares refinement are shown in Table I and the fractional atomic coordinates in Table II.

The structure is shown in Figure 1. The host molecule adopts a slightly distorted octahedral configuration, with all the N–Ni–N angles close to  $90^\circ$ . The average Ni–N bond length for the pyridine ligands is  $2.124(10) \text{ \AA}$  and that for the isothiocyanate ligands is  $2.064(8) \text{ \AA}$ . These are in good agreement with many previously reported bond lengths and angles in similar structures [8–14]. Thermal parameters and a list of bond lengths and bond angles have been deposited. The clathrating framework is formed by  $\text{Ni}(\text{NCS})_2(4\text{-PhPy})_4$  host molecules whose orientations determine the cavities which house the guest molecules. The DMSO guests lie in two distinct and crystallographically nonequivalent channels which are parallel to the  $z$ -axis.

### 2.2. $\text{Ni}(\text{NCS})_2(3\text{-MePy})_4 \cdot \text{CHCl}_3$ , II

The clathrate was prepared by dissolving the host complex in excess chloroform and heating to the boiling temperature. Suitable crystals were again mounted in capillaries. Refined cell dimensions and reflection data were collected as before and are reported in Table I. The origin was chosen at  $\bar{1}$  and the Ni atom, which lies on a diad at Wyckoff position  $f$ , was located by direct methods, while the other host atoms were found in subsequent electron density maps.

The guest molecules were, however, clearly disordered and considerable effort was spent

Table I. Crystal data and experimental and refinement parameters for the structures

Crystal data	I	II	III
Molecular formula	$C_{46}H_{36}N_6NiS_2 \cdot 4C_2H_6OS$	$C_{26}H_{28}N_6NiS_2 \cdot CHCl_3$	$C_{30}H_{36}N_6NiS_2$
$M_r$ (g mol <sup>-1</sup> )	1108.20	666.76	603.51
Space group	$P\bar{1}$	$Fddd$	$I4_1/acd$
$a$ (Å)	25.21(1)	26.28(1)	16.187(8)
$b$ (Å)	12.217(6)	24.35(1)	16.187(8)
$c$ (Å)	10.242(5)	21.47(1)	25.30(1)
$\alpha$ (deg)	111.35(2)	90	90
$\beta$ (deg)	84.12(2)	90	90
$\gamma$ (deg)	90.75(2)	90	90
$V$ (Å <sup>3</sup> )	2921.51	13739.04	6627.77
$Z$	2	16	8
$D_m$ (g cm <sup>-3</sup> )	1.24	1.31	1.22
$D_c$ (g cm <sup>-3</sup> )	1.27	1.29	1.20
$\mu$ (MoK $\alpha$ ) (cm <sup>-1</sup> )	36.26	61.29	61.25
$F(000)$	1164	5504	2544
Data Collection			
Crystal dimensions/mm	0.55 × 0.30 × 0.25	0.50 × 0.50 × 0.50	0.45 × 0.45 × 0.58
Scan mode	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
Scan width (deg $\theta$ )	0.70	1.60	0.40
Scan speed (deg $\theta$ s <sup>-1</sup> )	0.023	0.053	0.016
Range scanned (deg)	$3 < \theta < 23$	$3 < \theta < 23$	$3 < \theta < 23$
Stability of standard reflections (%)	1.4	2.6	1.1
Number of reflections collected	8077	2594	2623
Number of 'observed' reflections	5390	1324	978
Significance test		$I_{rel} > 2\sigma(I_{rel})$	
Final refinement			
Number of variables	321	97	103
$R = \Sigma \ F_o\  -  F_c\  / \Sigma  F_o $	0.131	0.121	0.101
$R_w = \Sigma w^{1/2} \ F_o\  -  F_c\  / \Sigma w^{1/2}  F_o $	0.120	0.133	—
Weighting scheme $w$	$(\sigma^2 F)^{-1}$	$(\sigma^2 F + 0.0088 F^2)^{-1}$	unit

in finding a suitable representation of the structure for refinement. The model finally adopted accounts for all six electron density peaks that appeared in the difference Fourier map and assumes that there are two 'half molecules' of  $CHCl_3$  that are statistically disordered. This is represented in Figure 2. In the final refinement, the H atoms of the host were subjected to constrained geometry and the C and H atoms were not included in the two 'halves' of the guest molecule, which had site occupancy of 0.56 and 0.44, respectively.

The geometry of the host molecule is unremarkable, with the nickel octahedrally coordinated to two *trans* thiocyanate moieties and four 3-methylpyridines. The bond lengths and angles lie within the expected ranges. The conformation of the 3-methylpyridines can be described by the torsion angles  $N(1)-Ni-N(x_1)-C(x_2)$  with  $x = 1,3$  and  $2,4$ , the pairs being related by the two-fold symmetry of the molecule, as shown in Figure 3. The angles have values of  $35.1^\circ$ ,  $-143.9^\circ$ ,  $-142.9^\circ$ ,  $36.3^\circ$  giving the host molecule a  $+ - + -$  conformation [14].

Table II. Compound I: fractional atomic coordinates ( $\times 10^4$ ) with e.s.d.'s in parentheses

Atom (host)	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Atom (host)	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ni(1)	2449(1)	1516(1)	3316(1)	C(44)	2387(4)	5864(9)	5559(11)
N(1)	2012(3)	1568(7)	1759(9)	C(45)	2539(4)	5271(10)	4110(12)
C(1)	1690(4)	1752(8)	1153(10)	C(46)	2533(4)	4038(10)	3517(12)
S(1)	1216(1)	1983(3)	268(4)	C(411)	2392(5)	7190(10)	6276(12)
N(2)	2907(3)	1567(7)	4914(9)	C(412)	2008(5)	7766(11)	7398(12)
C(2)	3269(4)	1590(9)	5535(11)	C(413)	2011(5)	9039(11)	8079(14)
S(2)	3785(1)	1558(3)	6328(4)	C(414)	2390(5)	9608(12)	7598(13)
N(11)	3168(3)	1507(7)	2019(9)	C(415)	2764(5)	9056(12)	6485(14)
C(12)	3632(4)	1956(10)	2473(12)	C(416)	2779(5)	7810(11)	5778(13)
C(13)	4116(5)	1823(10)	1625(12)	H(12)	3633(4)	2466(10)	3596(12)
C(14)	4127(4)	1173(9)	159(11)	H(13)	4473(5)	2211(10)	2087(12)
C(15)	3628(4)	753(10)	-370(12)	H(15)	3606(4)	307(10)	-1497(12)
C(16)	3175(4)	921(9)	573(11)	H(16)	2805(4)	576(9)	152(11)
C(111)	4613(5)	978(10)	-856(12)	H(112)	5026(6)	2412(13)	622(16)
C(112)	5046(6)	1702(13)	-411(16)	H(113)	5880(7)	1943(14)	-1095(17)
C(113)	5526(7)	1448(14)	-1418(17)	H(114)	5885(6)	528(13)	-3474(16)
C(114)	5539(6)	623(13)	-2720(16)	H(115)	5162(6)	-815(13)	-4119(15)
C(115)	5130(6)	-82(13)	-3104(15)	H(116)	4297(5)	-395(11)	-2495(13)
C(116)	4641(5)	133(11)	-2150(13)	H(22)	1807(5)	-571(10)	1469(11)
N(21)	2515(3)	-373(7)	2424(8)	H(23)	1860(5)	-2747(10)	418(12)
C(22)	2141(5)	-1024(10)	1643(11)	H(25)	3287(4)	-2607(10)	2361(11)
C(23)	2169(5)	-2265(10)	1044(12)	H(26)	3235(4)	-478(10)	3214(11)
C(24)	2596(4)	-2880(9)	1257(11)	H(212)	1814(5)	-4496(11)	198(12)
C(25)	2962(4)	-2187(10)	2100(11)	H(213)	1946(6)	-6671(12)	-899(13)
C(26)	2922(4)	-976(10)	2619(11)	H(214)	2805(6)	-7598(13)	-1228(14)
C(211)	2636(4)	-4174(9)	620(11)	H(215)	3563(7)	-6443(14)	-276(16)
C(212)	2204(5)	-4891(11)	106(12)	H(216)	3456(6)	-4247(13)	898(14)
C(213)	2282(6)	-6126(12)	-529(13)	H(32)	1221(4)	2230(9)	3728(11)
C(214)	2759(6)	-6649(13)	-685(14)	H(33)	403(4)	1915(9)	5073(11)
C(215)	3181(7)	-6015(14)	-180(16)	H(35)	1345(5)	61(10)	6852(12)
C(216)	3116(6)	-4761(13)	482(14)	H(36)	2138(5)	457(10)	5519(12)
N(31)	1732(3)	1363(7)	4536(8)	H(312)	-149(5)	2109(11)	6728(12)
C(32)	1250(4)	1756(9)	4420(11)	H(313)	-949(5)	1756(12)	8194(13)
C(33)	782(4)	1572(9)	5182(11)	H(314)	-937(5)	168(11)	9004(13)
C(34)	799(4)	959(9)	6051(11)	H(315)	-137(5)	-1044(12)	8621(14)
C(35)	1306(5)	544(10)	6174(12)	H(316)	674(5)	-759(11)	7061(13)
C(36)	1753(5)	771(10)	5409(12)	H(42)	2128(4)	3437(9)	6267(11)
C(311)	315(4)	735(9)	6881(11)	H(43)	2095(4)	5556(10)	7413(12)
C(312)	-135(5)	1416(11)	7136(12)	H(45)	2659(4)	5763(10)	3454(12)
C(313)	-594(5)	1200(12)	7954(13)	H(46)	2638(4)	3605(10)	2385(12)
C(314)	-583(5)	329(11)	8422(13)	H(412)	1711(5)	7269(11)	7757(12)
C(315)	-144(5)	-366(12)	8186(14)	H(413)	1716(5)	9515(11)	8948(14)
C(316)	326(5)	-179(11)	7331(13)	H(414)	2400(5)	10559(12)	8124(13)
N(41)	2408(3)	3366(7)	4243(9)	H(415)	3052(5)	9578(12)	6139(14)
C(42)	2249(4)	3952(9)	5639(11)	H(416)	3075(5)	7361(11)	4898(13)
C(43)	2232(4)	5152(10)	6296(12)				

Atom (guests)	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Atom (guests)	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Guest molecule 1				Guest molecule 3			
S(30)	8308(2)	4246(5)	855(9)	S(50)	9250(2)	3782(5)	5409(7)
O(30)	8808(5)	3683(10)	755(12)	O(50)	9761(5)	3725(12)	5856(14)

Table II (continued)

Atom (guests)	$x/a$	$y/b$	$z/c$	Atom (guests)	$x/a$	$y/b$	$z/c$
C(301)	9252(8)	5696(17)	1911(20)	C(501)	9041(7)	5287(16)	6078(19)
C(302)	9800(7)	3570(17)	1417(20)	C(502)	8744(8)	3161(19)	6217(22)
Guest molecule 2				Guest molecule 4			
S(40)	5665(3)	4186(7)	6851(9)	S(60)	4001(3)	6088(5)	7911(9)
O(40)	6119(5)	3464(12)	6596(14)	O(60)	4466(6)	6181(14)	7252(16)
C(401)	5497(13)	4840(28)	8573(34)	C(601)	3671(8)	4937(18)	6562(22)
C(402)	5159(9)	3221(20)	6091(23)	C(602)	3596(8)	7324(18)	8056(22)

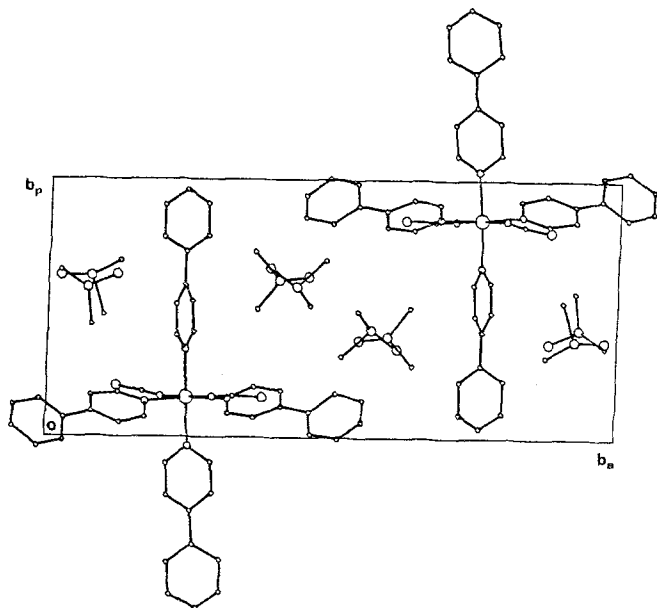
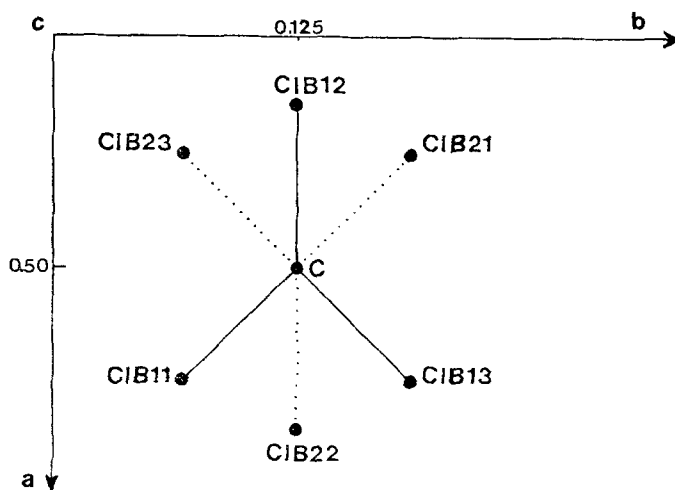


Fig. 1. Projection of structure I viewed along [001].

Fig. 2. Disordered  $\text{CHCl}_3$  guest in structure II.

The molecular packing is characterised by channels that are parallel to  $a$ . These have a rhomboidal cross-section and are shown in Figure 4. Fractional atomic coordinates are shown in Table III and tables of thermal parameters and molecular parameters have been deposited.

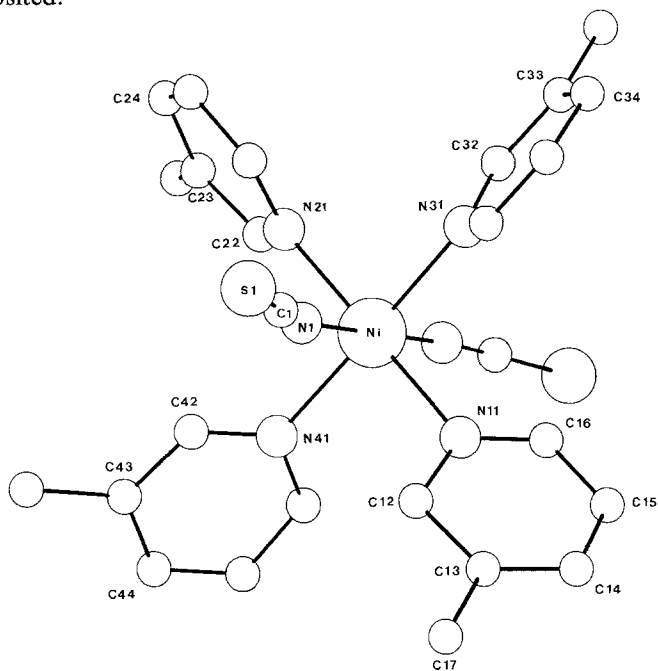


Fig. 3. Perspective view of host molecule of structure II with atomic nomenclature.

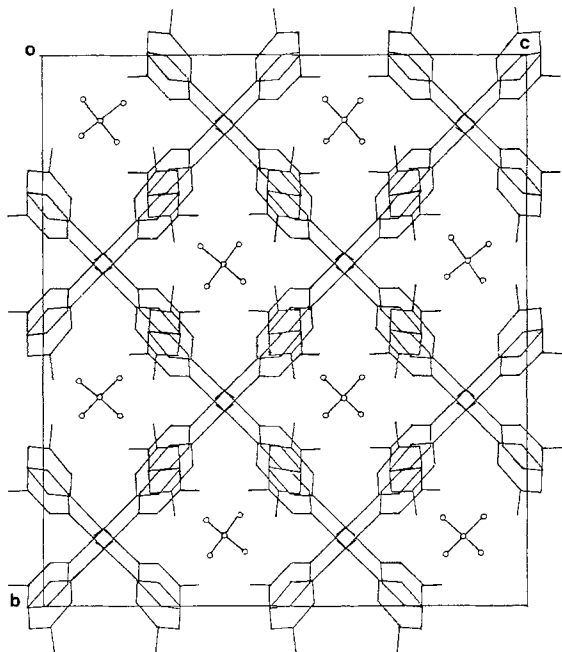


Fig. 4. Projection of structure II viewed along [100].

Table III. Compound II: fractional atomic coordinates ( $\times 10^4$ ) with e.s.d.'s in parentheses

Atom (host)	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Atom (host)	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ni(1)	1250(0)	3579(1)	1250(0)	C(26)	1552(7)	2920(7)	2397(8)
N(1)	2039(5)	3568(5)	1318(6)	C(27)	410(8)	1702(9)	2286(11)
C(1)	2449(5)	3692(6)	1401(6)	H(12)	1930(6)	3928(6)	140(7)
S(1)	3038(2)	3842(2)	1551(3)	H(14)	1351(7)	5329(8)	-649(9)
N(11)	1275(5)	4205(5)	553(6)	H(15)	667(8)	5313(9)	97(9)
C(12)	1661(6)	4218(6)	122(7)	H(16)	638(7)	4554(7)	816(8)
C(13)	1698(8)	4622(7)	-343(8)	H(171)	2467(9)	4482(10)	-663(12)
C(14)	1333(7)	5023(8)	-338(9)	H(172)	1958(9)	4423(10)	-1091(12)
C(15)	933(8)	5020(9)	91(9)	H(173)	2188(9)	5030(10)	-933(12)
C(16)	931(7)	4580(7)	520(8)	H(22)	619(6)	2561(6)	1553(7)
C(17)	2132(9)	4651(10)	-768(12)	H(24)	1154(7)	1836(8)	3152(8)
N(21)	1204(5)	2947(5)	1943(6)	H(25)	1807(8)	2488(8)	3174(9)
C(22)	863(6)	2555(6)	1911(7)	H(26)	1823(7)	3208(7)	2418(8)
C(23)	830(7)	2117(7)	2335(8)	H(271)	240(8)	1640(9)	1876(11)
C(24)	1175(7)	2120(8)	2817(8)	H(272)	611(8)	1369(9)	2401(11)
C(25)	1540(8)	2503(8)	2842(9)	H(273)	146(8)	1773(9)	2611(11)
Atom (guest)	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Atom (guest)	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Cl1A	2836(9)	4299(10)	4082(11)	Cl1B	2298(12)	3368(12)	4164(13)
Cl2A	1928(15)	3750(0)	3750(0)	Cl2B	3290(17)	3750(0)	3750(0)

2.3. Ni(NCS)<sub>2</sub>(3,5-diMePy)<sub>4</sub>, III

Several attempts at preparing a clathrate of the host compound with a variety of guest molecules (DMSO, CHCl<sub>3</sub>, *o*-, *p*- and *m*-xylene) failed. However, we pursued the structure analysis in order to obtain accurate atomic coordinates which could be used in a conformational study of the compound.

Suitable octahedral crystals were obtained from a DMSO solution of the compound and were stable in air. Crystal and reflection data are listed in Table I. The structure was routinely solved by vector methods and refined by full-matrix least-squares with Ni, S and all N and C atoms treated anisotropically. The H atoms were subjected to constrained refinement as described earlier.

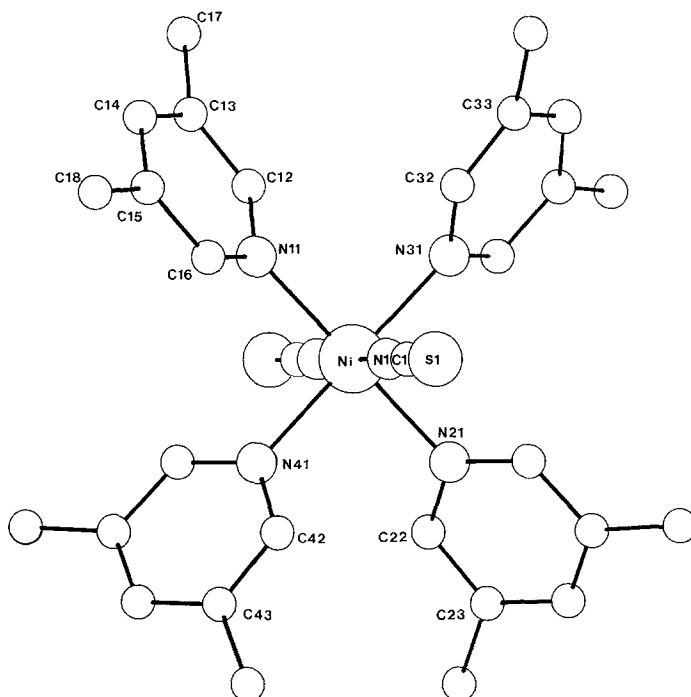
The tetragonal space group  $I4_1/acd$  has two choices of origin: the coordinates reported in Table IV are relative to the origin at  $\bar{4}$ . The Ni atom is at Wyckoff position *b* and the thiocyanate moieties lie on a diad at Wyckoff position *f*. The latter groups are thus constrained to linearity, an unusual feature in these compounds.

The lutidine groups lie on general positions and are essentially planar. The Ni atom is again octahedrally coordinated, with the NCS ligands in *trans* positions. The molecular parameters are unremarkable, with Ni-N distances and the angles about the Ni both in the expected ranges. The structure is similar to that of Ni(ClO<sub>4</sub>)<sub>2</sub>(3,5-diMePy)<sub>4</sub> elucidated by Madaule-Aubry and Brown [15]. This latter structure is pseudo isomorphous with that of compound III, the only difference being the replacement of the NCS ligand by ClO<sub>4</sub>, which is disordered about a diad.

The host molecule is shown in Figure 5, and the conformation of the lutidine moieties can again be described by the torsion angles N(1)-Ni-N(*x*<sub>1</sub>)-C(*x*<sub>2</sub>) *x* = 1,3 and 2,4. The values 136.5°, -43.5°, 136.5°, -43.5° are consistent with a + - + - conformation which is

Table IV. Compound **III**: fractional atomic coordinates ( $\times 10^4$ ) with e.s.d.'s in parentheses

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ni(1)	0000(0)	0000(0)	2500(0)	C(18)	2843(10)	-1099(11)	3463(6)
S(1)	2093(3)	2093(3)	2500(0)	H(12)	-425(8)	-934(9)	351(5)
N(1)	879(7)	879(7)	2500(0)	H(14)	1813(12)	-1705(10)	4224(5)
C(1)	1386(9)	1386(9)	2500(0)	H(16)	1807(9)	-424(8)	2766(5)
N(11)	654(8)	-652(7)	3099(3)	H(171)	693(13)	-2054(13)	4422(6)
C(12)	241(8)	-973(9)	3505(5)	H(172)	-346(13)	2038(13)	4631(6)
C(13)	649(12)	-1354(10)	3923(6)	H(173)	-	1103(13)	4529(6)
C(14)	1490(12)	-1400(10)	3905(5)	H(181)	190(13)	-701(11)	3798(6)
C(15)	1934(9)	-1078(10)	3493(6)	H(182)	2948(10)	1395(11)	3352(6)
C(16)	1478(9)	-697(8)	3093(5)	H(183)	3415(10)	-1564(11)	3566(6)
C(17)	112(13)	-1730(13)	4392(6)		2392(10)	-	

Fig. 5. Perspective view of host molecule of structure **III** with atomic nomenclature.

imposed by the crystallographic symmetry requirements. However, the 3,5-dimethylpyridine ligand is itself symmetrical, thereby yielding the equivalent + + + + conformation. These torsion angles are similar to those found in the pseudo-isomorphous  $\text{Ni}(\text{ClO}_4)_2(3,5\text{-diMePy})_4$  structure [15]. Thermal parameters and additional molecular parameters have been deposited.

### 3. Potential Energy Study

The theory of nonbonded interactions between molecules has received much attention in the last 20 years, and has recently been reviewed by Burkert and Allinger [18]. The shape of the



van der Waals potential function is characterised by the depth of the potential well, the corresponding equilibrium distance between the atoms and the steepness of the curve arising from repulsion at short distances.

We have carried out potential energy calculations of both intra- and intermolecular non-bonded interactions occurring in the three structures, using the technique of atom pair potentials. With the program EENY [16], we evaluated the van der Waals energy using atom-atom potentials of the form:

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

where  $r$  is the distance between any pair of atoms, and coefficients  $a$ ,  $b$ ,  $c$  and  $d$  are those given by Giglio [17]. These potential energy curves were derived primarily to give good agreement for calculations of molecular positions in crystal structure. No account is taken of partial atomic charges or dipole interactions, and the energy values derived mean little in an absolute sense.

Giglio's force field has been used successfully in a number of problems, including the intermolecular energy calculations in deoxycholic acid clathrates [19,20], the intramolecular conformations of a variety of compounds such as vitamin *U* hydrochloride [21], conformation patterns in cholanic acids [22], and the study of rotational motion of disordered perchlorate ions [23].

### 3.1 INTRAMOLECULAR ENERGY PROFILES

For compound I we have endeavoured to describe the shapes of the channels by calculating the potential energy environment of a 'probe molecule'. We chose a methyl group as a suitable probe and allowed this to move systematically throughout the unit cell while calculating its intermolecular interaction with the host molecules at suitable intervals. The unit cell was sliced into 20 sections along the  $z$ -direction and at each interval two-dimensional energy maps were evaluated and contoured at intervals of 10 Kcal. We found that the position of lowest energy corresponded closely to the location of the guest molecules as derived from the crystal structure. A perspective view of the channels, showing the surface of zero potential energy, is shown in Figure 6. We simulated the movement of a DMSO molecule through the channels by translating the molecule along the channel in steps of 0.51 Å, allowing it rotational freedom, and calculating the potential energy at each point. The resulting energy profiles showed no significant energy barriers in either channel, suggesting an unhindered motion of the guest molecules through the clathrate. The procedure was repeated for compound II and the energy profile was evaluated by passing a guest molecule through the channel, allowing it partial rotational freedom, and allowing the host molecules partial conformational freedom as well.

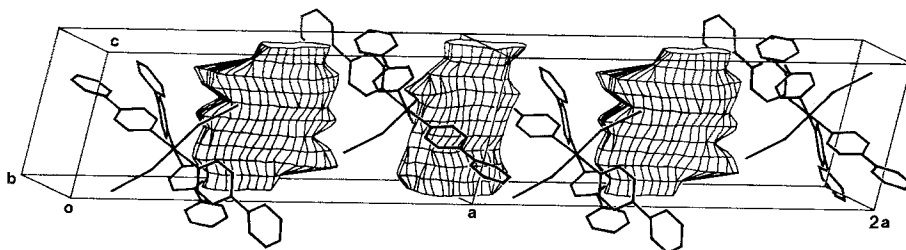


Fig. 6. Structure I: two unit cells depicting the host molecules and the zero-energy surfaces of the channels.

This was achieved by letting the 3-methylpyridine moieties twist about their Ni—N bonds. The final profile thus obtained, shown in Figure 7, has a maximum energy barrier of approximately 12 Kcal/mol which is similar to the value obtained for desorption studies of *p*-xylene from the 4-MePy complex [2].

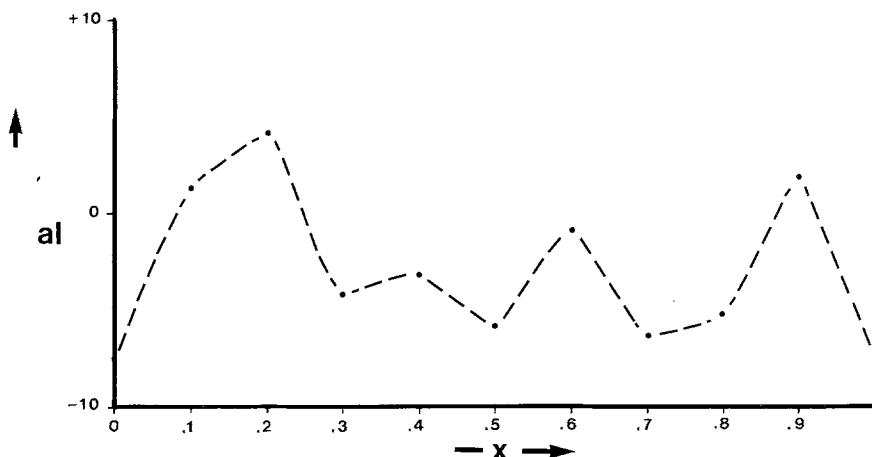


Fig. 7. Structure II: potential energy profile of a guest molecule moving through a channel.

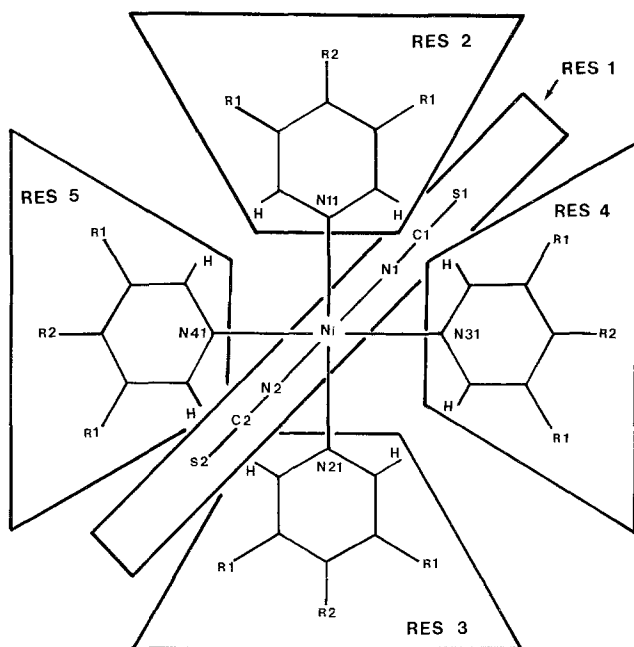
### 3.2. INTRAMOLECULAR CONFORMATIONAL STUDY: COMPOUND III

One of the main reasons advanced [2] to explain the versatility of these Werner clathrates is the rotational freedom of the substituted pyridines about their Ni—N bonds. This supposedly allows adjustment of the host molecules to accommodate a variety of guests, differing in size and shape. The geometries of the various cavities occurring in these clathrates is discussed in Lipkowsky's recent review [3]. It is intriguing, therefore, that the 3,5-dimethylpyridine compound has thus far defied attempts at clathrate formation, while the 4-methylpyridine analogue does so readily.

We have, therefore, carried out an intramolecular conformational energy study of both of these compounds. The molecule of compound **III** was divided into five residues linked by four torsion angles as shown in Figure 8, with  $R_1 = \text{Me}$  and  $R_2 = \text{H}$ .

Energy maps of the interaction between the linear S—C—N—Ni—N—C—S residue and the four lutidines were then computed, allowing the four bases to twist about their Ni—N bonds. The torsion angles, N—Ni—N( $x_1$ )—C( $x_2$ ), with  $x = 1, 3$  and  $2, 4$ , were initially set at the crystal-structure values and the resulting pseudo-five-dimensional layer diagram showing the variation of energy as a function of torsion angles is displayed in Figure 9. The amount of rotational flexibility can then be judged by the extent of the energy contours shown on the map.

We repeated the study but changed the bases to 4-methylpyridine ( $R_1 = \text{H}$ ,  $R_2 = \text{Me}$  in Figure 8) and obtained a pseudo-five-dimensional layer diagram which was almost identical to that shown in Figure 9. Careful analysis of the intramolecular close contacts which occur upon torsion of the four substituted pyridines, shows that the energy is almost exclusively governed by the two *ortho*-hydrogens on each base. It is these which control the extent to which the substituted pyridines may turn, while the variation of substituents at the *meta* and *para* positions makes only a secondary contribution. These potential energy studies yielded the lowest energy at torsion angles very close to those found in the crystal structure. This study



R1 = Me ; R2 = H

OR

R1 = H ; R2 = Me

Fig. 8. Schematic representation of structure III divided into residues.

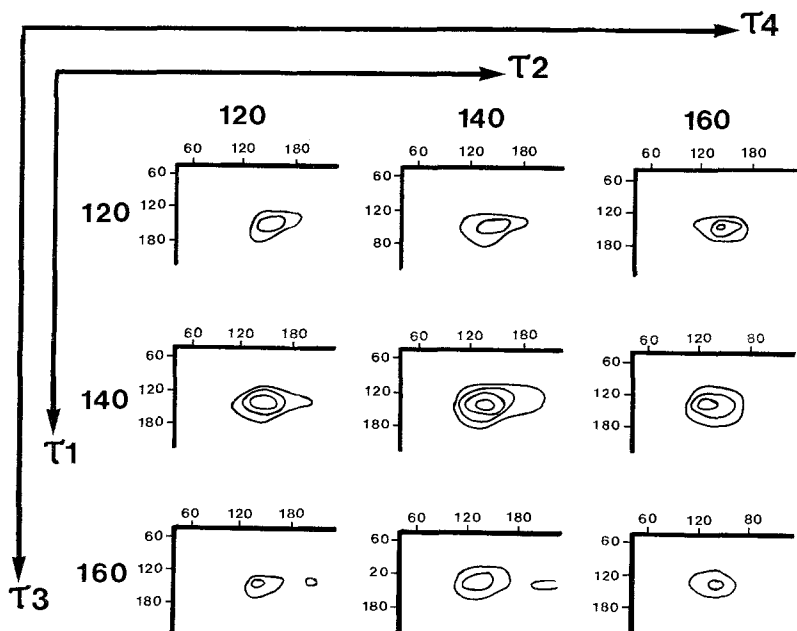


Fig. 9. Pseudo-five-dimensional potential energy map. Contours are at 0, -2, -4 ... Kcal.

is similar to that carried out by Lipkowski [14] on  $\text{Ni}(\text{NCS})_2(4\text{-MePy})_4$ , except that in the latter only the N–Ni–N subunit was used as the linear residue 1 (Figure 8).

The extent of rotation allowed by the 3,5-dimethylpyridines is, therefore, not the factor which governs clathrate formation; other factors must be found to explain the failure of compound III to form inclusion compounds.

## Acknowledgements

We thank the CSIR (Pretoria) for the diffractometer data collections and the CSIR and the University of Cape Town for research grants.

## References

1. W. D. Schaeffer, W. S. Dorsey, D. A. Skinner, and C. G. Christian: *J. Am. Chem. Soc.* **79**, 5870 (1956).
2. J. Lipkowski: *Accademia Polacca delle Scienze (Roma), Conferenze* **81** (1980).
3. J. Lipkowski: in *Inclusion Compounds*, vol. 1, chapter 3 (eds. J. L. Atwood, J. E. D. Davies, and D. D. MacNicol), Academic Press, London (1984).
4. J. Lipkowski, P. Starzewski, and W. Zielenkiewicz: *Pol. J. Chem.* **56**, 349 (1982).
5. W. Kemula, D. Sybliska, and J. Lipkowski: *J. Chromatogr.* **218**, 465 (1981).
6. D. R. Bond, G. E. Jackson, and L. R. Nassimbeni: *S. Afr. J. Chem.* **36**, 19 (1983).
7. G. M. Sheldrick: *Computing in Crystallography*, Delft University Press, Delft, Holland (1978).
8. J. Lipkowski, K. Suwinska, G. D. Andreetti, and K. Stadnicka: *J. Mol. Struct.* **75**, 101 (1981).
9. G. D. Andreetti, *J. Mol. Struct.* **75**, 129 (1981).
10. J. Lipkowski, P. Sgarabotto, and G. D. Andreetti: *Acta Crystallogr.* **B36**, 51 (1980).
11. J. Lipkowski, G. D. Andreetti, and P. Sgarabotto: *Acta Crystallogr.* **A34**, S145 (1978).
12. G. D. Andreetti, L. Cavalca, and P. Sgarabotto: *Gazz. Chim. Ital.* **100**, 697 (1970).
13. A. Lewartowska, S. Brzozowski, and W. Kemula: *J. Mol. Struct.* **75**, 113 (1981).
14. J. Lipkowski: *J. Mol. Struct.* **75**, 13 (1981).
15. F. Madaule-Aubry and G. M. Brown: *Acta Crystallogr.* **B24**, 745 (1968).
16. W. D. S. Motherwell: 'EENY Potential Energy Program', Cambridge University.
17. E. Giglio: *Nature* **222**, 339 (1969).
18. U. Burkert and N. L. Allinger: *Molecular Mechanics*, A.C.S. Monograph 177 (1982).
19. S. Candeloro De Sanctis and E. Giglio: *Acta Crystallogr.* **B35**, 2650 (1979).
20. E. Giglio: *J. Mol. Struct.* **75**, 39 (1981).
21. G. Del Re, E. Gavuzzo, E. Giglio, F. Leij, F. Mazza, and V. Zappia: *Acta Crystallogr.* **B33**, 3289 (1977).
22. E. Giglio and C. Quagliata: *Acta Crystallogr.* **B31**, 743 (1975).
23. W. Fedeli, F. Mazza, E. Giglio, C. Quagliata, and N. Scarcelli: *Acta Crystallogr.* **B32**, 878 (1976).