Studies in Werner Clathrates. Part 9.[1] Structures with Bis(isothiocyanato)-tetrakis(4-phenylpyridine)nickel(II) as Host†

Luigi R. Nassimbeni,* Margaret L. Niven, and Michael W. Taylor
Department of Physical Chemistry, University of Cape Town, Rondebosch 7700, South Africa

The structures of the Werner clathrates with the host complex $[Ni(NCS)_2(4\text{-}Phpy)_4]$ (4-Phpy = 4-phenylpyridine) and mixed guests (4-phenylpyridine + dimethyl sulphoxide), (4-phenylpyridine + 2-methoxyethanol), and (phenylacetylene + dimethyl sulphoxide) have been elucidated. The packing of these three complexes has been compared. Trends in the torsion angles of the host molecules of the complexes and of $[Ni(NCS)_2(4\text{-}Phpy)_4]\cdot m\text{-}MeC_6H_4Me$ are discussed and their importance to the process of clathration highlighted.

Werner clathrates are inclusion compounds comprising host molecules having the general formula MX_2L_4, where M is a divalent transition-metal cation (*e.g.* Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, *etc.*), X is an anionic ligand (*e.g.* NCS^-, NCO^-, halide, *etc.*), and L is a neutral substituted pyridine or α-arylalkylamine. These compounds have the ability to enclose a wide variety of organic compounds as guest molecules. They were discovered by Schaeffer *et al.*[2] who studied their ability to separate aromatic compounds. The most stable clathrates of this type are formed by the host $[Ni(NCS)_2(4\text{-}Mepy)_4]$ (4-Mepy = 4-methylpyridine), and their structures and physical properties have been reviewed by Lipkowski.[3]

We have synthesized and characterised the clathrates obtained by the host $[Ni(NCS)_2(4\text{-}vpy)_4]$ (4-vpy = 4-vinylpyridine) with *o*-, *m*-, *p*-xylenes, and chloroform, and have studied their thermal decomposition.[4,5] From the structural point of view, the most versatile host is $[Ni(NCS)_2(4\text{-}Etpy)_4]$ (4-Etpy = 4-ethylpyridine) which forms clathrates which crystallise in a wide variety of space groups, and their structures depend on the geometry of the guest molecules as well as the host:guest ratio.[6]

Recently we have studied the clathrates formed with $[Ni(NCS)_2(4\text{-}Phpy)_4]$ (4-Phpy = 4-phenylpyridine) as host compound, and its clathrates with *o*- and *m*-xylene, and *p*-xylene with dimethyl sulphoxide.[1] The 4-phenylpyridine ligand is particularly interesting in that it has torsional flexibility about the pyridine–phenyl bond, an important factor in clathrate formation. We now report the clathrate structures of $[Ni(NCS)_2(4\text{-}Phpy)_4]$ with 4-Phpy + dmso, **(1)**, 4-Phpy + 2-methoxyethanol, **(2)**, and phenylacetylene + dmso, **(3)**, (dmso = dimethyl sulphoxide).

Experimental

The host complex, in powder form, was prepared by dissolving stoicheiometric amounts of $NiCl_2\cdot 6H_2O$ and K(SCN) in water and adding an excess of 4-phenylpyridine dissolved in a minimum of ethanol. The precipitate formed was continuously stirred for two hours before filtration and drying.

Clathrates **(1)** and **(3)** were prepared by dissolving the host complex in hot (60 °C) dmso and layering the solution with 4-phenylpyridine dissolved in methanol and phenylacetylene respectively. Clathrate **(2)** was prepared by dissolving the host in 2-methoxyethanol and layering with 4-phenylpyridine dissolved in methanol. Suitable single crystals were obtained after allowing these layered solutions to stand at room temperature for 2 weeks.

Crystallography.—Single crystals were cut to suitable size and immediately mounted in Lindemann tubes together with the mother liquor, to avoid rapid deterioration through guest desorption. Density measurements were carried out by flotation in mixtures of water and saturated KI solution, and measuring the density of the solution by means of a PAAR DMA 35 density meter.

Intensity Data Collection.—All intensity data were collected at 294 K on a Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.710 7 Å). Accurate cell parameters were obtained by least-squares analysis of several high-θ reflections. In all cases, scans were in the ω–2θ mode, with a final acceptance limit of 20σ at 20° min^{-1} in ω, and a maximum recording time of 50 s [**(1)** and **(2)**] and 40 s [**(3)**]. The vertical aperture width was fixed at 4 mm and for each structure: (*i*) the aperture width was set according to (x + 1.05tanθ) mm; (*ii*) the scan width, in ω, was set according to

Table 1. Experimental and refinement parameters for the structures

Compound	**(1)**	**(2)**	**(3)**
Crystal dimensions/mm	0.38 × 0.31 × 0.25	0.19 × 0.19 × 0.31	0.47 × 0.44 × 0.38
θ range scanned/°	1—25	1—23	1—20
Average transmission/%	78		
Crystal stability/%	3.1	7.5	8.0
Scan width	0.74	1.44	1.04
Aperture width	1.35	1.56	1.35
Total no. of reflections	6 540	4 561	2 973
Total no. observed	3 059[a]	2 569[a]	1 945[b]
No. of variables	305	302	161
R^c	0.106 7	0.107 3	0.107 4
R'^d	0.105 7	0.091 5	0.104 3
Weighting scheme, w	$(\sigma^2F)^{-1}$	$(\sigma^2F)^{-1}$	$(\sigma^2F + 0.01F^2)^{-1}$

[a] $I_{rel} > 2\sigma I_{rel}$. [b] $I_{rel} > 4\sigma I_{rel}$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$.

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

($y + 0.35\tan\theta$)°. Table 1 lists values of scan and aperture widths for each structure.

For each data collection the intensities of three reference reflections were periodically monitored to check crystal stability. All intensities were corrected for Lorentz and polarisation factors, but an empirical absorption correction was only applied to compound (**1**) owing to the crystal decay of compounds (**2**) and (**3**). Crystal data and experimental details are listed in Tables 1 and 2.

Structure Solution.—All structures were solved using the heavy-atom method with the SHELX 86 program system.[7] Refinement was carried out by full-matrix least squares using the SHELX 76 program.[8] The solution and refinement of the host structure and of the aromatic guest, *i.e.* 4-phenylpyridine for compounds (**1**) and (**2**) and phenylacetylene for compound (**3**), proved to be routine in all three cases, with the guest atoms appearing unequivocally in a difference electron density map.

Table 2. Crystal data for the clathrates (**1**), (**2**), and (**3**)

Compound	(1)	(2)	(3)
Guest 1 (G1)	4-Phpy	4-Phpy	PhC≡CH
Guest 2 (G2)	dmso	$MeOCH_2CH_2OH$	dmso
H:G1:G2 ratio	1:1:1	1:1:1	1:2:1
M/g mol^{-1}	1 029	1 027	1 077
D_m/g cm^{-3}	1.235	1.242	1.209
D_c/g cm^{-3}	1.23	1.24	1.19
μ(Mo-K_α)/cm^{-1}	4.18	4.34	3.95
F(000)	1 688	2 072	2 152
Space group	$P2_1/n$	$P2_1/n$	$C2/c$
a/Å	10.150(5)	10.085(3)	10.065(7)
b/Å	24.073(5)	23.723(4)	24.147(8)
c/Å	23.049(14)	23.266(7)	24.743(11)
β/°	98.62(4)	99.17(3)	94.00(6)
U/Å^3	5 568.2	5 495.2	5 998.0
Z	4	4	4

Density measurements of the crystals had indicated that a mixed-guest clathrate was possible. This was confirmed when the host–aromatic guest model failed to refine beneath an R value of 0.15 and peaks of several e Å^{-3} were revealed in residual space from an electron density map. Attempts to fit a model of dmso to the remaining electron density peaks for compounds (**1**) and (**3**) proved to be unsuccessful. Use was made of spherically averaged scattering factors (g) as described by Jones *et al.*[9] to model the dmso, with atomic co-ordinates for dmso, including all H atoms, taken from the crystal-structure determination of Thomas *et al.*[10] The spherically averaged molecular scattering factor was represented in computations by the function: $g = 31.8\exp(-52.06s^2) + 3.2\exp(-2.4s^2) + 1.2\exp(-1.15s^2) + 5.8$, where $s = \sin\theta/\lambda$. Use of this g function in a difference Fourier synthesis led to a significant reduction in R, for both compounds (**1**) and (**3**), and also accounted for all the remaining electron density peaks. Although the model of dmso had very high thermal parameters, *ca.* 0.3 Å^2, its inclusion was felt to be justified to describe the behaviour of the aliphatic guest molecule.

For compound (**2**) a molecule of two-fold, statistically disordered 2-methoxyethanol (see Figure 1) was obtained from a contoured electron density map. Refinement as a rigid

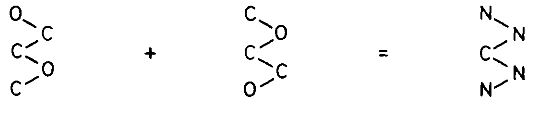


Figure 1. Schematic diagrams showing a two-fold, statistically disordered molecule of 2-methoxyethanol

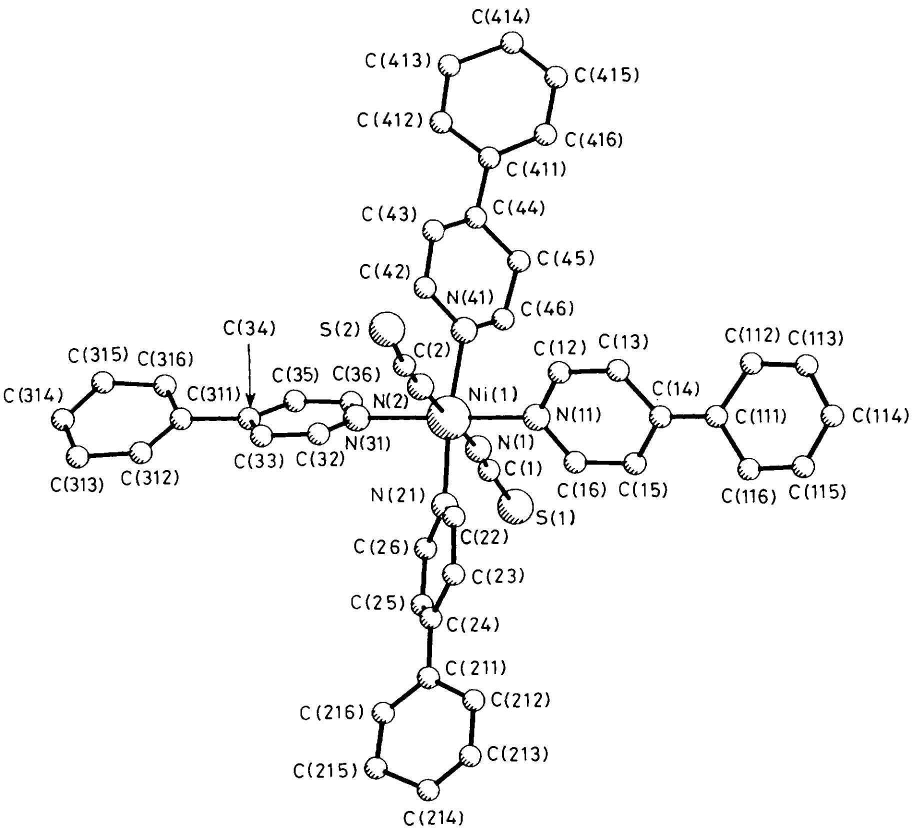


Figure 2. Perspective view of a typical host molecule with atomic numbering scheme

molecule accounted for all electron density peaks greater than 1 e Å^{-3}. Owing to statistical disorder of the 2-methoxyethanol molecule, the average atomic scattering factors of the carbon and oxygen atoms, excepting the central carbon atom, were approximated as the atomic scattering factor of the nitrogen atom.

Final refinement of all three compounds involved full-matrix least squares with Ni and S atoms of the host treated anisotropically and hydrogen atoms geometrically positioned and linked with common thermal parameters. Complex neutral-atom scattering factors for hydrogen were taken from Stewart *et al.*[11] and for all other atoms from Cromer and Mann.[12] For

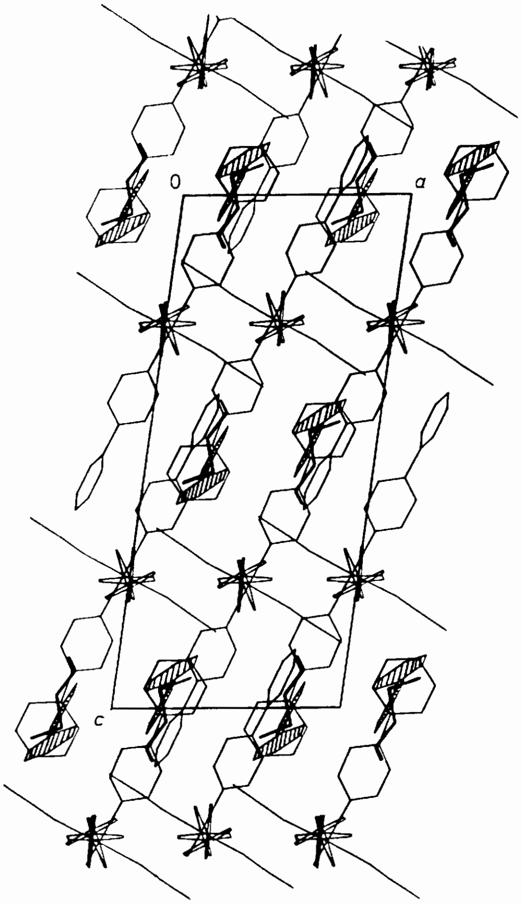


Figure 3. Projection of compound (**2**) viewed along [010], with guest molecules shaded

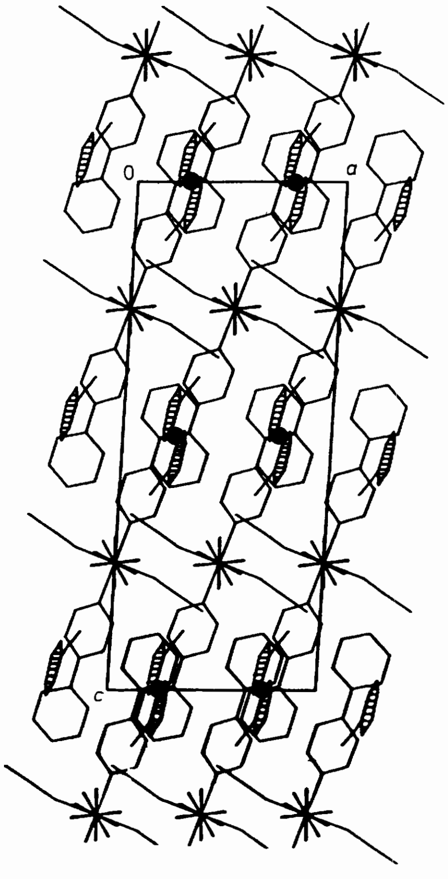
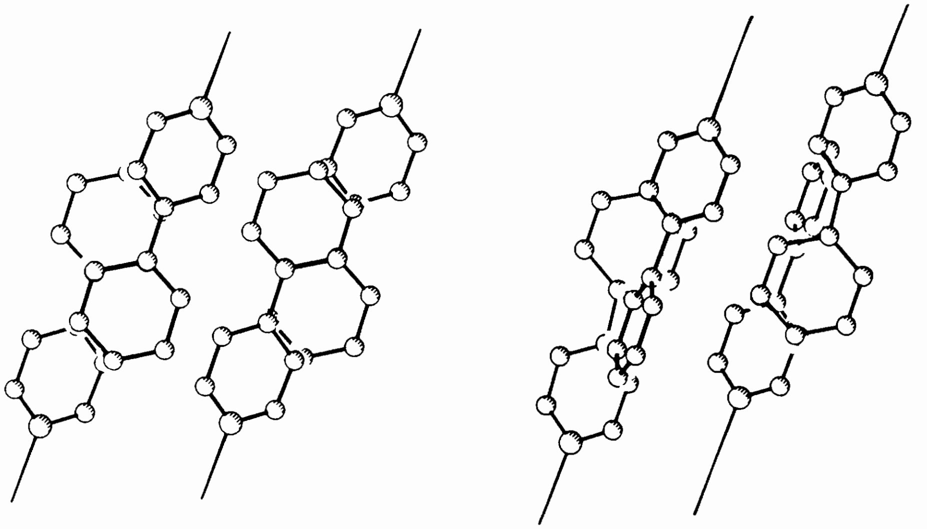


Figure 4. Projection of compound (**3**) viewed along [010] with guest molecules shaded. Solid circles represent dmso



(*a*) (*b*)

Figure 5. (*a*) Packing about Wyckoff position *c* for compound (**3**). (*b*) Analogous position for compound (**2**). Both viewed along [010] with guest molecules omitted

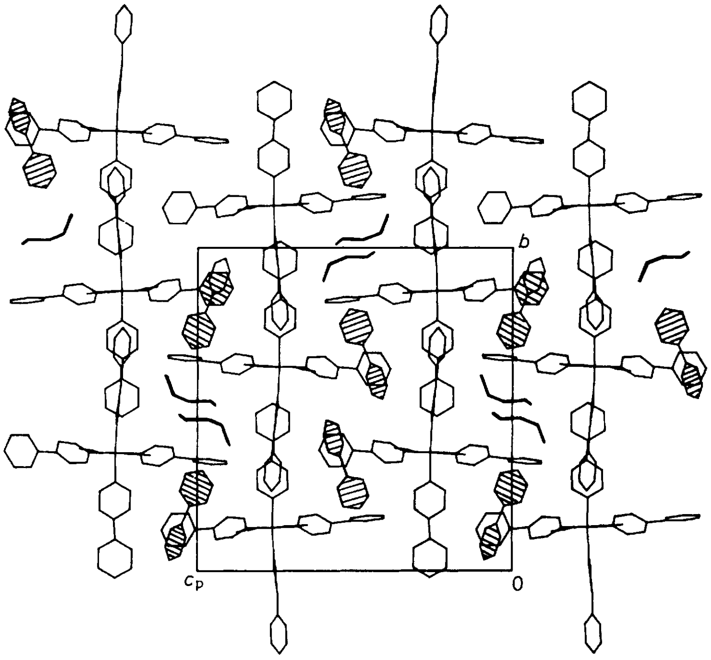


Figure 6. Projection of compound (**2**) viewed along [100] with guest molecules shaded

Table 3. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for compound (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni(1)	−308(2)	3 487(1)	2 387(1)	C(35)	−2 685(18)	3 126(7)	3 782(8)
N(1)	1 596(14)	3 381(5)	2 800(6)	C(36)	−2 146(16)	3 194(7)	3 269(8)
C(1)	2 543(17)	3 425(7)	3 092(8)	C(311)	−2 389(13)	3 308(6)	4 877(5)
S(1)	3 933(7)	3 480(4)	3 564(3)	C(312)	−1 459(13)	3 258(6)	5 386(5)
N(2)	−2 268(13)	3 557(6)	1 966(6)	C(313)	−1 889(13)	3 211(6)	5 931(5)
C(2)	−3 355(16)	3 590(6)	1 787(7)	C(314)	−3 249(13)	3 214(6)	5 967(5)
S(2)	−4 913(5)	3 597(2)	1 516(3)	C(315)	−4 178(13)	3 264(6)	5 459(5)
N(11)	348(12)	3 541(5)	1 546(6)	C(316)	−3 748(13)	3 310(6)	4 915(5)
C(12)	1 386(18)	3 269(8)	1 400(9)	N(41)	−89(13)	4 371(5)	2 477(6)
C(13)	1 838(16)	3 319(7)	866(8)	C(42)	1 092(17)	4 637(7)	2 456(8)
C(14)	1 195(16)	3 680(7)	452(8)	C(43)	1 215(17)	5 196(7)	2 490(8)
C(15)	135(17)	3 949(8)	575(9)	C(44)	100(15)	5 524(7)	2 525(7)
C(16)	−307(17)	3 876(8)	1 123(8)	C(45)	−1 085(17)	5 261(7)	2 542(8)
C(111)	1 648(13)	3 742(6)	−126(5)	C(46)	−1 151(17)	4 681(7)	2 520(8)
C(112)	2 160(13)	3 299(6)	−413(5)	C(411)	213(12)	6 147(4)	2 547(5)
C(113)	2 575(13)	3 383(6)	−958(5)	C(412)	1 206(12)	6 413(4)	2 291(5)
C(114)	2 476(13)	3 911(6)	−1 213(5)	C(413)	1 261(12)	6 991(4)	2 279(5)
C(115)	1 962(13)	4 353(6)	−926(5)	C(414)	323(12)	7 305(4)	2 520(5)
C(116)	1 549(13)	4 268(6)	−383(5)	C(415)	−668(12)	7 040(4)	2 776(5)
N(21)	−457(12)	2 617(5)	2 310(6)	C(416)	−723(12)	6 462(4)	2 789(5)
C(22)	63(18)	2 288(8)	2 754(9)	C(11G)	3 033(17)	7 670(5)	−85(8)
C(23)	97(18)	1 725(8)	2 736(9)	C(12G)	3 585(17)	7 238(5)	−372(8)
C(24)	−435(15)	1 435(7)	2 232(7)	C(13G)	3 588(17)	6 699(5)	−150(8)
C(25)	−1 050(16)	1 799(7)	1 760(8)	C(14G)	3 040(17)	6 592(5)	359(8)
C(26)	−988(15)	2 357(7)	1 827(7)	C(15G)	2 489(17)	7 026(5)	645(8)
C(211)	−487(12)	824(4)	2 177(6)	C(16G)	2 486(17)	7 564(5)	422(8)
C(212)	−27(12)	498(4)	2 666(6)	C(21G)	3 009(18)	4 930(5)	1 009(8)
C(213)	−27(12)	−78(4)	2 619(6)	C(22G)	1 948(18)	5 288(5)	1 052(8)
C(214)	−485(12)	−331(4)	2 082(6)	C(23G)	1 973(18)	5 832(5)	842(8)
C(215)	−944(12)	−5(4)	1 591(6)	C(24G)	3 060(18)	6 015(5)	589(8)
C(216)	−946(12)	572(4)	1 640(6)	C(25G)	4 120(18)	5 658(5)	545(8)
N(31)	−996(12)	3 432(6)	3 209(6)	C(26G)	4 094(18)	5 115(5)	756(8)
C(32)	−350(17)	3 660(7)	3 700(8)	S(1G)	3 117(17)	117(6)	301(6)
C(33)	−740(18)	3 625(7)	4 239(9)	S(2G)	−2 888(21)	1 294(8)	553(8)
C(34)	−1 918(17)	3 376(7)	4 314(8)				

Table 4. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for compound (**2**)

Atom	*x*	*y*	*z*
Ni(1)	280(3)	3 667(2)	2 600(2)
N(1)	2 222(23)	3 667(10)	3 049(10)
C(1)	3 218(27)	3 755(11)	3 346(11)
S(1)	4 677(9)	3 803(5)	3 729(4)
N(2)	−1 710(19)	3 629(9)	2 169(8)
C(2)	−2 718(25)	3 619(11)	1 875(11)
S(2)	−4 129(8)	3 586(4)	1 488(5)
N(11)	1 026(21)	3 634(10)	1 800(10)
C(12)	2 138(25)	3 341(11)	1 730(12)
C(13)	2 545(26)	3 260(11)	1 213(13)
C(14)	1 906(28)	3 531(12)	725(13)
C(15)	698(22)	3 830(10)	788(11)
C(16)	358(29)	3 896(12)	1 330(13)
C(111)	2 215(23)	3 465(8)	128(8)
C(112)	3 577(23)	3 381(8)	108(8)
C(113)	4 012(23)	3 302(8)	−425(8)
C(114)	3 088(23)	3 306(8)	−939(8)
C(115)	1 727(23)	3 390(8)	−920(8)
C(116)	1 291(23)	3 469(8)	−386(8)
N(21)	296(21)	2 752(8)	2 595(11)
C(22)	751(25)	2 476(12)	3 088(12)
C(23)	707(22)	1 890(11)	3 095(11)
C(24)	97(24)	1 593(10)	2 639(12)
C(25)	−350(23)	1 900(12)	2 135(12)
C(26)	−268(21)	2 477(11)	2 126(11)
C(211)	5(17)	972(6)	2 593(11)
C(212)	41(17)	690(6)	3 121(11)
C(213)	−20(17)	102(6)	3 132(11)
C(214)	−115(17)	−201(6)	2 613(11)
C(215)	−150(17)	80(6)	2 085(11)
C(216)	−91(17)	668(6)	2 075(11)
N(31)	−462(19)	3 689(10)	3 429(9)
C(32)	121(28)	3 958(12)	3 870(13)
C(33)	−296(27)	4 028(12)	4 400(13)
C(34)	−1 394(26)	3 680(14)	4 468(13)
C(35)	−2 014(28)	3 354(12)	4 034(13)
C(36)	−1 537(27)	3 376(12)	3 497(13)
C(311)	−1 899(19)	3 729(12)	5 046(8)
C(312)	−1 862(19)	4 228(12)	5 367(8)
C(313)	−2 288(19)	4 230(12)	5 908(8)
C(314)	−2 752(19)	3 735(12)	6 129(8)
C(315)	−2 791(19)	3 236(12)	5 810(8)
C(316)	−2 365(19)	3 233(12)	5 269(8)
N(41)	190(22)	4 550(8)	2 556(10)
C(42)	1 291(25)	4 869(12)	2 510(11)
C(43)	1 271(27)	5 438(12)	2 473(12)
C(44)	67(23)	5 741(10)	2 435(11)
C(45)	−1 112(28)	5 410(12)	2 481(12)
C(46)	−1 017(30)	4 820(13)	2 562(13)
C(411)	−6(18)	6 362(6)	2 433(8)
C(412)	928(18)	6 661(6)	2 171(8)
C(413)	859(18)	7 247(6)	2 138(8)
C(414)	−148(18)	7 534(6)	2 366(8)
C(415)	−1 084(18)	7 236(6)	2 626(8)
C(416)	−1 014(18)	6 648(6)	2 659(8)
C(11G)	2 020(21)	6 896(7)	174(11)
C(12G)	2 489(21)	6 991(7)	−350(11)
C(13G)	2 582(21)	7 540(7)	−556(11)
C(14G)	2 207(21)	7 994(7)	−237(11)
C(15G)	1 741(21)	7 899(7)	287(11)
C(16G)	1 646(21)	7 352(7)	493(11)
C(21G)	2 536(34)	9 667(8)	−877(12)
C(22G)	1 544(34)	9 530(8)	−547(12)
C(23G)	1 436(34)	8 979(8)	−350(12)
C(24G)	2 322(34)	8 564(8)	−485(12)
C(25G)	3 313(34)	8 703(8)	−816(12)
C(26G)	3 421(34)	9 254(8)	−1 013(12)
N(1G)	2 115(27)	6 049(12)	1 009(11)
N(2G)	1 776(34)	5 464(14)	776(15)
C(3G)	2 448(36)	5 273(18)	275(13)
N(4G)	2 039(34)	5 288(16)	−375(13)
N(5G)	3 300(53)	5 126(33)	−569(22)

compounds (**1**) and (**2**), the host and guest molecules lie in general positions but for compound (**3**), with $Z = 4$, the nickel atom and two pyridine ligands are situated on the diad at Wyckoff position *e*.

The final fractional atomic co-ordinates of all three structures are given in Tables 3—5. Figure 2 gives a perspective view of a typical host molecule with the atomic numbering scheme.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Discussion

The structure of the complexes in all three compounds has the central nickel atom in an octahedral configuration with the isothiocyanate moieties in *trans* positions. The observed bond lengths and angles are within accepted limits for compounds of this type.[6]

The host compound $[Ni(NCS)_2(4\text{-}Phpy)_4]$ has previously displayed a wide variety in packing upon forming a clathrate, crystallising in several space groups,[1] unlike the 4-vinylpyridine analogue, which frequently forms clathrates in the tetragonal space group $I4_1/a$.[4] Packing of the host compound in all three structures is very similar, with the guest molecules occupying corresponding regions in the unit cell. Figures 3 and 4 show the packing of the structures of compounds (**2**) and (**3**) respectively, both viewed along [010].

The space group $P2_1/n$ [compounds (**1**) and (**2**)] is a subset of the space group $C2/c$ [compound (**3**)]. It is the extra symmetry elements in the centred space group that cause the major differences in the packing for these compounds. The centre of symmetry at Wyckoff *c* in compound (**3**) causes the ligands lying around it to pack parallel to each other. When this centre is absent the individual ligands gain some conformational freedom. This difference is highlighted in Figure 5 which shows this region, with the guest molecule absent for clarity, for compounds (**2**) and (**3**).

Rotational freedom about the Ni–N bonds is a possible reason for the formation of clathrates by these kinds of inorganic complexes. The 4-phenylpyridine compounds under discussion have four extra rotational parameters of the phenyl rings with respect to their parent pyridines. The four torsion angles relating to rotation about $Ni\text{–}N_{py}$ bonds are described by: N(1)–Ni–N(x1)–C(x2) with $x = 1(\tau_1)$, $x = 2(\tau_3)$, $x = 3(\tau_5)$, and $x = 4(\tau_7)$, and their corresponding intraligand torsion angles as: C(y3)–C(y4)–C(y11)–C(y12), with $y = 1(\tau_2)$, $y = 2(\tau_4)$, $y = 3(\tau_6)$, and $y = 4(\tau_8)$. For these three compounds and for the compound $[Ni(NCS)_2(4\text{-}Phpy)_4]\cdot m\text{-}MeC_6H_4Me$,[1] because the packing is similar, it has been possible to ensure consistency when labelling the ligands.

In compounds (**1**) and (**2**) the guest molecules are located in channels running parallel to *a*. The 4-phenylpyridine guests occupy one set of channels at $y = z = 0$, while the aliphatic guests occupy the second set of channels at $y = 0$, $z = \frac{1}{2}$. The packing of compound (**2**), viewed along [100] is shown in Figure 6.

In compound (**3**) the phenylacetylene molecules lie on either

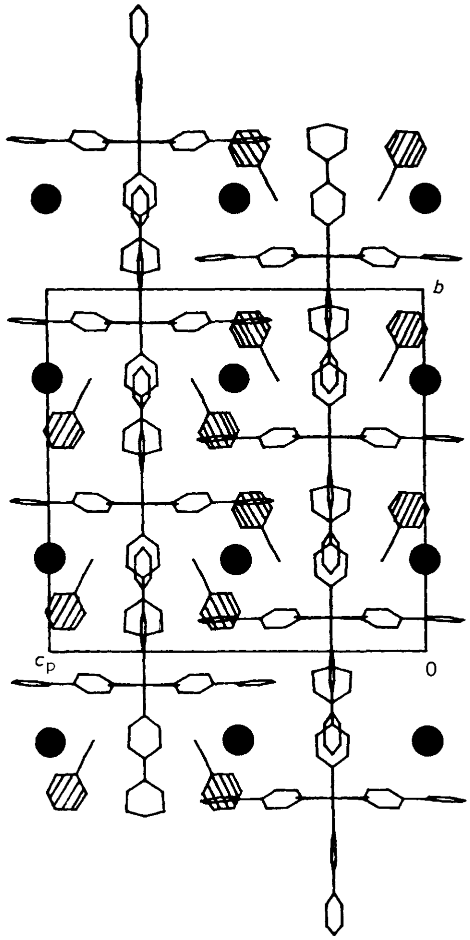


Figure 7. Projection of compound (**3**) viewed along [100] with guest molecules shaded. Filled circles represent dmso

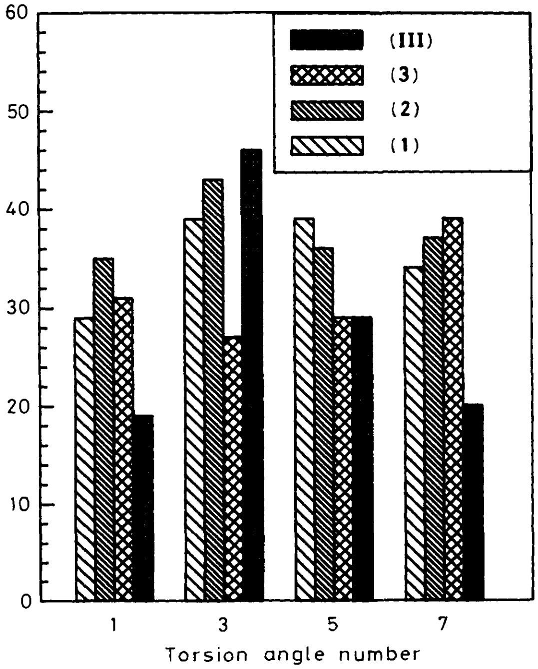


Figure 8. Histogram of pyridine torsion angles

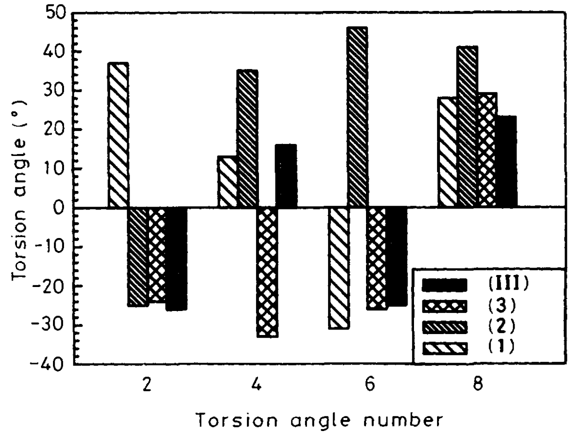


Figure 9. Histogram of phenyl torsion angles

Table 5. Fractional atomic co-ordinates ($\times 10^4$) with e.s.d.s in parentheses for compound (**3**)

Atom	*x*	*y*	*z*
Ni(1)	0	924(1)	2 500
S(1)	4 336(4)	937(2)	3 453(2)
N(1)	1 954(10)	937(4)	2 804(4)
C(1)	2 947(12)	932(4)	3 084(5)
N(11)	645(9)	899(4)	1 704(4)
C(12)	1 793(12)	1 140(5)	1 569(5)
C(13)	2 223(12)	1 149(5)	1 036(5)
C(14)	1 457(11)	895(4)	630(5)
C(15)	280(13)	634(6)	765(5)
C(16)	−89(12)	656(5)	1 303(5)
C(111)	1 822(11)	883(4)	55(5)
C(112)	3 174(14)	946(5)	−42(6)
C(113)	3 502(17)	930(6)	−584(7)
C(114)	2 545(17)	848(6)	−1 007(7)
C(115)	1 221(14)	802(6)	−899(6)
C(116)	883(13)	833(5)	−350(5)
N(21)	0	45(5)	2 500
C(22)	1 135(12)	−260(5)	2 456(5)
C(23)	1 167(12)	−802(5)	2 440(5)
C(24)	0	−1 118(7)	2 500
C(211)	0	−1 722(8)	2 500
C(212)	1 064(19)	−2 016(8)	2 703(7)
C(213)	997(26)	−2 613(10)	2 708(9)
C(214)	0	−2 857(16)	2 500
N(41)	0	1 791(5)	2 500
C(42)	617(12)	2 090(5)	2 897(5)
C(43)	648(12)	2 663(5)	2 932(5)
C(44)	0	2 976(7)	2 500(0)
C(411)	0	3 577(7)	2 500(0)
C(412)	68(12)	3 887(5)	2 974(5)
C(413)	38(12)	4 435(5)	3 002(5)
C(414)	0	4 576(4)	2 500
C(12G)	1 502(28)	7 476(13)	1 153(10)
C(11G)	1 943(22)	7 893(10)	924(8)
C(1G)	2 329(16)	8 413(7)	689(7)
C(2G)	2 397(23)	8 953(10)	955(10)
C(3G)	2 817(22)	9 384(10)	670(10)
C(4G)	3 031(25)	9 356(12)	121(11)
C(5G)	2 965(22)	8 905(10)	−93(9)
C(6G)	2 646(17)	8 410(8)	143(7)
S(1G)	2 500	2 500	0

side of the centres of inversion located at Wyckoff position *a*, while the disordered dmso molecules lie at Wyckoff position *c*. Together they form an undulating channel running parallel to *b* at $z = \frac{1}{2}$. This is shown in Figure 7 which views the packing along [100].

We have calculated all the non-bonded distances between the guests and the host framework. There are more than 50 interactions whose interatomic distances are less than 3.5 Å, and it is clear that the ring systems on the host molecules have twisted in order to accommodate the guests. We have compared the torsion angles of the rings of these three compounds as well as those of the *m*-xylene structure [labelled compound **(III)**]. These are shown in Figures 8 and 9. The pyridine torsion angles are all in the range 19—46°, consistent with the + + + + propeller conformation often found in Werner clathrates.[3] The phenyl torsion angles, however, can be positive or negative, and no pattern could be discerned. Presumably each moiety twists in order best to accommodate its particular guest.

Acknowledgements

We thank the University of Cape Town, the Council for Scientific and Industrial Research (Pretoria), and African Explosives and Chemical Industries (Modderfontein) for research grants.

References

1 Part 7, L. R. Nassimbeni, M. L. Niven, and M. W. Taylor, *Inorg. Chim. Acta*, 1987, **132**, 67; Part 8, L. R. Nassimbeni, M. L. Niven, and A. P. Suckling, *ibid.*, submitted for publication.
2 W. D. Schaeffer, W. S. Dorsey, D. A. Skinner, and J. Christian, *J. Am. Chem. Soc.*, 1957, **79**, 5870.
3 J. Lipkowski, in 'Inclusion Compounds,' eds. J. L. Atwood, J. E. D. Davies, and D. D. MacNicol, Academic Press, London, 1984, vol. 1, ch. 3.
4 M. H. Moore, L. R. Nassimbeni, M. L. Niven, and M. W. Taylor, *Inorg. Chim. Acta*, 1986, **115**, 211.
5 M. H. Moore, L. R. Nassimbeni, and M. L. Niven, *Inorg. Chim. Acta*, 1987, **131**, 45.
6 M. H. Moore, L. R. Nassimbeni, and M. L. Niven, *J. Chem. Soc., Dalton Trans.*, 1987, 2125.
7 G. M. Sheldrick, in 'Crystallographic Computing 3,' eds. G. M. Sheldrick, C. Kruger, and R. Goddard, Oxford University Press, Oxford, 1985, p. 175.
8 G. M. Sheldrick, in 'Computing in Crystallography,' eds. H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld, and G. C. Bassi, Delft University Press, Delft, 1978, p. 34.
9 J. G. Jones, S. Schwarzbaum, and L. Lessinger, *Acta Crystallogr., Sect. B*, 1982, **38**, 1207.
10 R. Thomas, C. B. Shoemaker, and K. Eriks, *Acta Crystallogr.*, 1966, **21**, 12.
11 R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
12 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 1968, **24**, 321.

Received 22nd January 1988; *Paper* 8/00346G