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Studies in Werner Clathrates.
Part 7. Structures of Bis(isothiocyanato)tetrakis(4-phenylpyridine)nickel(II) and its Clathrates with *ortho*-Xylene, *meta*-Xylene and *para*-Xylene + Dimethylsulphoxide

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Abstract

The crystal structures of the α-phase [Ni(NCS)$_2$-(4-PhPy)$_4$] (**I**), Werner complex and of its clathrating form with *o*-xylene (**II**), *m*-xylene (**III**) and *p*-xylene + DMSO (**IV**) have been elucidated. The [Ni(NCS)$_2$-(4-PhPy)$_4$] molecules in all four structures have a 'propeller' conformation of the pyridine rings and nickel is octahedrally coordinated. The clathrating phases show the guest molecules lying in well defined channels.

Introduction

The field of inorganic coordination compounds as clathrating agents was started by Schaeffer *et al.* who showed that these compounds could be used to separate various aromatic hydrocarbons from petroleum fractions [1].

The compound which has been most thoroughly studied thus far is [Ni(NCS)$_2$(4-MePy)$_4$], which forms clathrates with a variety of aromatic compounds as 'guest' molecules.

The structures and thermodynamics of the clathration process with this compound as 'host' molecule have recently been reviewed [2, 3]. We have investigated the structural and stability changes which occur with variations in the pyridine ligand. We have thus elucidated the structures of the host [Ni(NCS)$_2$(4Vi-Py)$_4$] and its clathrates with the isomers of xylene [4], and have reported the structures of what is probably the most versatile host molecule of this kind, [Ni(NCS)$_2$(4EtPy)$_4$], which forms inclusion compounds of varying stoichiometry with carbon tetrachloride, carbon disulphide and the isomers of xylene [5]. Werner clathrates with chiral ligands, which are potentially useful in separating enantiomers, have also been recently studied and their structures reported [6].

We now report the structures of the 4-phenyl derivative [Ni(NCS)$_2$(4-PhPy)$_4$] in its non-porous or α-phase, and as the 'host' in the clathrating phase structures of its clathrates with *o*-xylene, *m*-xylene and *p*-xylene + DMSO.

Experimental Procedure and Structure Solutions

The host complex **I** was prepared by dissolving stoichiometric amounts of Ni(NO$_3$)$_2$·6H$_2$O and KSCN in methanol and allowing the solution to stir overnight. The precipitate of KNO$_3$ was filtered off and a stoichiometric amount of 4-phenylpyridine dissolved in a minimum of methanol was added dropwise. Small blue needle shaped crystals formed after three days of slow evaporation of the resulting green solution. The clathrate compounds with *ortho*- (**II**), *meta*- (**III**), and *para*-xylene (**IV**) were prepared by dissolving the host compound, synthesized by the method of Schaeffer *et al.* [1], in hot DMSO and layering with the respective xylene. Blue plate like crystals formed after 10–14 days.

For all structural determinations, which were carried out at 293 K, small crystals were cut and mounted in Lindemann capillaries with mother liquor to prevent desorption of the guest.

Preliminary cell parameters and space group symmetry were determined photographically. Accurate cell parameters were then obtained by least-squares analysis of twenty-five reflections measured in the range $16° < \theta < 17°$ on a Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). During the intensity data collection of each structure three reference reflections were periodically monitored to check crystal stability. Crystal data and experimental details of the data collections are listed in Table I. All data were corrected for Lorentz polarization factors and an empirical absorption correction was carried out on compounds **III** and **IV**.

The structures were solved by the heavy-atom method and refined by full-matrix least-squares using the SHELX76 [7] program system.

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TABLE I. Crystal Data, Experimental and Refinement Parameters for the Structures

Compound	**I**	**II**	**III**	**IV**
Crystal data				
Molecular formula	$C_{46}H_{36}N_6Ni_1S_2$	$C_{62}H_{56}N_6NiS_2$	$C_{62}H_{56}N_6NiS_2$	$C_{58}H_{58}N_6NiO_2S_4$
M_r (g mol^{-1})	795.7	1008.1	1008.1	1058.1
Space group	*Pbca*	*Fdd*2	*C*2/*c*	$P\bar{1}$
a (Å)	12.846(7)	10.376(10)	10.610(5)	10.149(13)
b (Å)	16.160(2)	44.414(20)	23.181(14)	12.234(38)
c (Å)	39.377(8)	23.436(50)	22.950(4)	27.014(8)
α (°)	90	90	90	99.60(13)
β (°)	90	90	99.63(4)	95.27(7)
γ (°)	90	90	90	111.55(16)
v (Å^3)	8174.3	10800.2	5565.1	3032.8
z	8	8	4	2
$H:G_1:G_2$	–:–:–	1:2:–	1:2:–	1:1:2
D_m (g cm^{-3})	1.29	1.26	1.18	1.21
D_c (g cm^{-3})	1.29	1.24	1.20	1.16
μ (Mo Kα) (cm^{-1})	5.67	4.37	4.24	3.85
F(000)	3312	4239.9	2120	859
Data collection				
Crystal dimensions (mm)	0.12 × 0.16 × 0.18	0.47 × 0.25 × 0.25	0.31 × 0.38 × 0.47	0.28 × 0.28 × 0.47
Scan mode	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
Scan width $\Delta\omega$ (°)	$0.84 + 0.35 \tan\theta$	$0.74 + 0.35 \tan\theta$	$0.74 + 0.35 \tan\theta$	$0.78 + 0.35 \tan\theta$
Vertical aperture length (mm)	6	4	4	4
Aperture width (mm)	$1.25 + 1.05 \tan\theta$	$1.15 + 1.05 \tan\theta$	$1.11 + 1.05 \tan\theta$	$1.13 + 1.05 \tan\theta$
Final acceptance limit	20σ at 20° min^{-1}	20σ at 20° min^{-1}	20σ at 20° min^{-1}	20σ at 20° min^{-1}
Max. recording time (s)	80	50	40	40
Total no. unique reflections	7948	2135	5174	10874
Crystal stability (%)	0.2	10.0	3.2	3.4
2θ range (°)	2–50	2–50	2–50	2–50
Final refinement				
No. variables	226	160	155	310
Total no. observed reflections	1788[a]	1697[b]	3037	6724
R[c]	0.9000	0.1286	0.0915	0.1267
R_w[d]	0.0691	0.1259	0.0894	0.1289
Weighting scheme	$(\sigma^2F)^{-1}$	$(\sigma^2F)^{-1}$	$(\sigma^2F)^{-1}$	$(\sigma^2F)^{-1}$
Average transmission (%)	–	–	98.35	95.74

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

Crystals of **I** were very small and weakly diffracting, with only 1788 out of 7984 being taken as significant, and we deemed an absorption correction unnecessary for this structure. The final refinement for **I** was carried out with Ni and S atoms treated anisotropically and with the H atoms constrained to 1.08 Å from their parent C atoms, with a common temperature factor.

Crystals of **II** suffered from severe decay during the data collection despite their being sealed in a Lindemann capillary. We therefore could not carry out a meaningful absorption correction on this data set. For **II**, the nickel and two 4-phenylpyridine rings are on the diad at Wyckoff position *a*. The nickel and sulphur were treated anisotropically and the H atoms geometrically placed as before. The guest molecule which is in a general position, emerged from the difference electron density map once all the host atoms had been located. Although *Fdd*2 is a polar space group, the data was too poor to allow us to determine the absolute configuration of the crystal structure.

For **III**, there being only four host molecules in the unit cell, they must be located on a special position. The Patterson located the Ni atom on Wyckoff position *e*, on the diad, and the Ni, S and H atoms were refined as before. There was no apparent disorder in the guest molecule although its isotropic temperature factors were all considerably higher than those of the aromatic carbon atoms in the host molecule.

The host molecule for **IV** was treated as described above but accurate location of the guest molecules proved to be difficult. Difference electron density

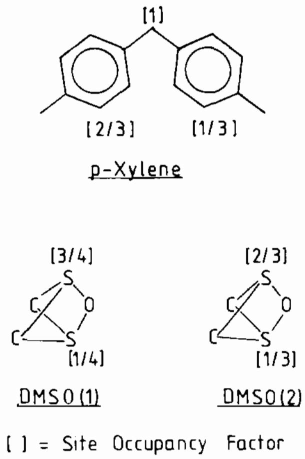

Fig. 1. Schematic diagrams showing the models of the disordered guest molecules in **IV**.

maps indicated that both the *p*-xylene and the DMSO molecules are disordered. The model of this disorder which yielded the best refinement is shown in Fig. 1.

The final fractional atomic coordinates and temperature factors of all four structures are given in Tables II–V.

Discussion

The structure of the complexes in all four compounds has the central nickel atom in an octahedral configuration with the isothiocyanate moieties in *trans* configuration. The observed bond lengths and angles around the nickel are within the accepted limits for compounds of this kind [4] (see 'Supplementary Material').

A perspective view of a molecule of **I**, the α-phase, is shown in Fig. 2. The host molecules of the other compounds are essentially similar. One of the possible reasons to explain the formation of clathrates by these kinds of inorganic complexes is the rotational freedom about the Ni–N bonds. This supposedly allows adjustment of substituted pyridines to accommodate the various guest molecules. In the case of the

TABLE II. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^3$) of Compound **I** (e.s.d.s in parentheses)

Atom	x/a	y/b	z/c	U_{iso}
Ni(1)	774(2)	364(1)	1353(0)	[a]
N(1)	1212(9)	1504(9)	1534(3)	67(4)
C(1)	1420(11)	2094(10)	1681(4)	55(5)
S(1)	1755(4)	2942(3)	1865(1)	[a]
N(2)	346(9)	−770(8)	1159(3)	60(4)
C(2)	−54(11)	−1360(10)	1053(3)	50(5)
S(2)	−576(4)	−2191(3)	900(1)	[a]
N(11)	2262(9)	219(8)	1136(3)	63(4)
C(12)	2751(12)	853(10)	975(3)	64(5)
C(13)	3711(13)	772(11)	813(4)	74(6)
C(14)	4229(13)	5(10)	827(4)	69(5)
C(15)	3723(12)	−621(10)	1014(4)	71(5)
C(16)	2759(12)	−498(10)	1158(3)	58(5)
C(111)	5282(8)	−85(8)	674(3)	76(6)
C(112)	5516(8)	336(8)	374(3)	147(8)
C(113)	6461(8)	193(8)	210(3)	174(10)
C(114)	7171(8)	−371(8)	345(3)	113(7)
C(115)	6937(8)	−792(8)	645(3)	153(9)
C(116)	5992(8)	−649(8)	809(3)	129(8)
N(21)	197(9)	945(7)	906(3)	51(4)
C(22)	−386(12)	1635(9)	948(4)	61(5)
C(23)	−990(11)	1967(9)	683(4)	56(5)
C(24)	−1042(12)	1594(9)	361(4)	56(5)
C(25)	−389(11)	886(9)	331(4)	57(5)
C(26)	173(12)	586(10)	600(4)	64(5)
C(211)	−1712(13)	1893(9)	94(4)	56(5)
C(212)	−2690(14)	2217(11)	179(4)	88(6)
C(213)	−3372(16)	2469(11)	−83(5)	98(7)
C(214)	−3109(15)	2391(11)	−421(5)	91(6)
C(215)	−2133(14)	2069(10)	−488(4)	84(6)
C(216)	−1437(13)	1822(9)	−249(4)	68(5)
N(31)	−752(10)	521(7)	1561(3)	55(3)
C(32)	−882(13)	967(9)	1841(4)	58(5)
C(33)	−1864(12)	1168(9)	1977(4)	62(5)
C(34)	−2772(11)	934(9)	1800(4)	46(4)
C(35)	−2603(12)	454(10)	1510(3)	64(5)
C(36)	−1606(12)	255(10)	1404(4)	67(5)
C(311)	−3832(11)	1193(8)	1906(4)	44(3)
C(312)	−4005(13)	1437(9)	2243(4)	79(6)
C(313)	−4959(15)	1750(11)	2341(4)	89(7)
C(314)	−5771(15)	1796(10)	2104(4)	81(5)
C(315)	−5606(14)	1584(10)	1777(4)	80(6)
C(316)	−4615(13)	1250(10)	1673(4)	80(6)
N(41)	1258(9)	−190(8)	1810(3)	58(4)
C(42)	2117(12)	28(9)	1992(4)	58(5)
C(43)	2333(11)	−289(9)	2305(3)	52(4)
C(44)	1625(12)	−834(8)	2458(4)	45(4)
C(45)	755(12)	−1071(8)	2279(3)	55(4)
C(46)	598(12)	−737(9)	1959(4)	59(5)
C(411)	1834(12)	−1187(9)	2799(4)	50(4)
C(412)	2837(12)	−1417(9)	2912(4)	60(5)
C(413)	2987(14)	−1755(10)	3229(4)	76(6)
C(414)	2183(13)	−1877(10)	3437(4)	78(6)
C(415)	1186(14)	−1677(10)	3337(4)	81(6)
C(416)	983(13)	−1306(9)	3019(4)	70(5)

[a] Anisotropic atoms have thermal parameters of the form: $T = \{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*) \times 10^3\}$, with the following parameters. Ni(1): U_{11}, 56(1); U_{22}, 49(1); U_{33}, 57(1); U_{23}, −6(1); U_{13}, −1(2); U_{12}, −3(1). S(1): U_{11}, 76(4); U_{22}, 57(3); U_{33}, 143(5); U_{23}, −34(3); U_{13}, −17(4); U_{12}, −11(3). S(2): U_{11}, 84(4); U_{22}, 76(4); U_{33}, 94(4); U_{23}, −35(3); U_{13}, 6(3); U_{12}, −19(3).

TABLE III. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^3$) of Compound **II** (e.s.d.s in parentheses)

Atom	x/a	y/b	z/c	U_{iso}
Ni(1)	0(0)	0(0)	0(0)	a
N(1)	−1649(16)	−273(3)	−5(9)	44(2)
C(1)	−2377(19)	−433(4)	21(10)	42(4)
S(1)	−3523(7)	−702(2)	−26(5)	a
N(11)	−1203(15)	396(3)	−58(8)	37(3)
C(12)	−2230(22)	390(5)	−309(10)	50(6)
C(13)	−3115(20)	647(5)	−386(10)	46(5)
C(14)	−2758(19)	906(4)	−46(10)	39(4)
C(15)	−1591(23)	909(5)	222(11)	55(6)
C(16)	−833(20)	651(4)	246(9)	39(4)
C(111)	−3659(20)	1170(4)	−103(10)	46(5)
C(112)	−4140(20)	1263(5)	−630(10)	50(5)
C(113)	−4954(23)	1516(5)	−661(11)	56(6)
C(114)	−5130(25)	1691(6)	−220(11)	60(7)
C(115)	−4616(28)	1599(6)	380(13)	76(8)
C(116)	−3769(22)	1353(5)	381(11)	55(6)
N(21)	0(0)	0(0)	957(17)	85(11)
C(22)	−1139(23)	13(5)	1176(10)	57(6)
C(23)	−1169(23)	19(5)	1763(10)	57(6)
C(24)	0(0)	0(0)	2059(15)	42(8)
C(211)	0(0)	0(0)	2763(12)	27(7)
C(212)	−981(25)	118(5)	3050(12)	62(6)
C(213)	−1030(25)	133(6)	3687(11)	65(7)
C(214)	0(0)	0(0)	3968(20)	70(12)
N(41)	0(0)	0(0)	−908(8)	17(4)
C(42)	−191(17)	−255(4)	−1226(8)	27(4)
C(43)	−223(21)	−265(5)	−1826(10)	47(5)
C(44)	0(0)	0(0)	−2174(13)	34(7)
C(411)	0(0)	0(0)	−2749(18)	64(12)
C(412)	434(21)	−258(5)	−3094(10)	48(5)
C(413)	444(25)	−244(6)	−3652(12)	72(7)
C(414)	0(0)	0(0)	−3929(26)	98(16)
CG(1)	2067(25)	874(6)	2009(12)	59(7)
CG(2)	3192(23)	1046(5)	2120(11)	55(6)
CG(3)	3712(27)	1061(6)	2649(11)	69(7)
CG(4)	3190(26)	899(5)	3086(12)	58(6)
CG(5)	2114(28)	736(6)	3040(14)	77(8)
CG(6)	1532(24)	731(5)	2471(13)	64(6)
CG(11)	1350(29)	837(6)	1451(13)	81(6)
CG(21)	3788(36)	1223(8)	1617(17)	121(12)

[a] Anisotropic atoms have thermal parameters of the form: $T = \exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hka^*c^* + 2U_{12}hla^*b^*) \times 10^{*3}\}$, with the following parameters. Ni(1): U_{11}, 35(2); U_{22}, 31(2); U_{33}, 39(2); U_{23}, 0(0); U_{13}, 0(0); U_{12}, 0(2). S(1): U_{11}, 67(4); U_{22}, 69(4); U_{33}, 113(7); U_{23}, 10(5); U_{13}, −7(5); U_{12}, −23(4).

TABLE IV. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^3$) of Compound **III** (with e.s.d.s in parentheses)

Atom	x/a	y/b	z/c	U_{iso}
Ni(1)	0(0)	2927(1)	2500(0)	a
N(1)	1857(6)	2896(3)	2935(3)	56(2)
C(1)	2778(7)	2859(3)	3273(3)	51(2)
S(1)	4078(2)	2791(1)	3743(1)	a
N(11)	664(5)	2979(3)	1668(3)	55(2)
C(12)	1847(8)	2827(3)	1596(4)	70(2)
C(13)	2329(8)	2943(4)	1084(4)	73(2)
C(14)	1600(7)	3214(3)	0612(3)	54(2)
C(15)	384(8)	3386(4)	698(4)	78(2)
C(16)	−50(8)	3256(3)	1219(4)	73(2)
C(111)	2064(8)	3356(3)	60(4)	64(2)
C(112)	3349(9)	3439(4)	44(5)	94(3)
C(113)	3747(11)	3612(5)	−484(5)	118(3)
C(114)	2878(10)	3675(4)	−1001(5)	95(3)
C(115)	1625(9)	3575(4)	−992(4)	90(3)
C(116)	1215(8)	3418(4)	−469(4)	73(2)
N(21)	0(0)	2013(4)	2500(0)	54(2)
C(22)	464(7)	1715(3)	2991(4)	64(2)
C(23)	472(7)	1114(3)	3002(4)	65(2)
C(24)	0(0)	802(5)	2500(0)	57(3)
C(211)	0(0)	147(6)	2500(0)	77(3)
C(212)	162(11)	−138(5)	3006(6)	131(4)
C(213)	176(13)	−754(6)	3010(7)	166(5)
C(214)	0(0)	−998(9)	2500(0)	142(7)
N(31)	0(0)	3837(4)	2500(0)	55(2)
C(42)	1095(7)	4155(3)	2580(3)	64(2)
C(43)	1131(8)	4748(3)	2592(4)	65(2)
C(44)	0(0)	5061(5)	2500(0)	52(2)
C(411)	0(0)	5692(5)	2500(0)	54(2)
C(412)	1061(7)	6000(3)	2385(3)	60(2)
C(413)	1070(8)	6599(4)	2385(4)	74(2)
C(414)	0(0)	6894(5)	2500(0)	74(3)
CG(11)	2499(11)	1394(6)	4616(6)	124(4)
CG(12)	3041(10)	991(5)	4268(5)	107(3)
CG(13)	3165(12)	423(6)	4395(6)	125(4)
CG(14)	2741(12)	182(6)	4899(6)	146(5)
CG(15)	2202(14)	610(8)	5235(7)	158(5)
CG(16)	2118(11)	1155(6)	5080(6)	121(4)
CG(17)	3755(13)	−15(7)	4044(7)	222(7)
CG(18)	1743(17)	370(8)	5725(9)	317(12)

[a] Anisotropic atoms have thermal parameters of the form: $T = \exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*) \times 10^3\}$, with the following parameters. Ni(1): U_{11}, 40(1); U_{22}, 58(1); U_{33}, 49(1); U_{23}, 0(0); U_{13}, 0(1); U_{12}, 0(0). S(1): U_{11}, 69(2); U_{22}, 131(3); U_{33}, 97(2); U_{23}, −24(2); U_{13}, −31(2); U_{12}, 24(2).

4-phenyl pyridine compounds under discussion, there are the added parameters of the four torsion angles describing the conformation of the phenyl rings with respect to their parent pyridines.

We have labelled the torsion angles as N(1)–Ni–N(x1)–C(x2) with $x = 1(\tau_1)$, $x = 2(\tau_3)$, $x = 3(\tau_5)$, $x = 4(\tau_7)$ 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 $y = 4(\tau_8)$. In each structure, the labelling of the ligands was carried out cyclically, and each compound was initially arbitrarily labelled. However, in order to carry out meaningful comparison of the structures, we systematically searched for the combination of torsion

TABLE V. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^3$) of Compound **IV** (with e.s.d.s in parentheses)

Atom	x/a	y/b	z/c	U_{iso}
Ni(1)	2120(2)	4506(1)	2329(1)	[a]
N(1)	606(11)	4657(9)	2765(4)	54(2)
C(1)	158(13)	4912(11)	3127(5)	49(3)
S(1)	−472(5)	5250(4)	3633(1)	[a]
N(2)	3664(10)	4275(8)	1906(4)	47(2)
C(2)	4229(12)	3966(10)	1603(4)	43(3)
S(2)	5025(5)	3511(4)	1165(2)	[a]
N(11)	3010(10)	6428(9)	2411(4)	50(2)
C(12)	3013(14)	7203(12)	2826(5)	57(3)
C(13)	3562(13)	8410(11)	2891(5)	54(3)
C(14)	4205(13)	8934(11)	2516(5)	47(3)
C(15)	4265(13)	8137(11)	2082(5)	52(3)
C(16)	3668(13)	6937(11)	2034(5)	51(3)
C(111)	4877(13)	10277(11)	2570(5)	50(3)
C(112)	5250(16)	11060(14)	3052(6)	81(4)
C(113)	5909(18)	12335(16)	3098(7)	98(5)
C(114)	6225(16)	12780(14)	2675(6)	76(4)
C(115)	5862(15)	12074(13)	2208(6)	74(4)
C(116)	5178(14)	10816(12)	2140(5)	61(3)
N(21)	775(10)	4394(8)	1648(4)	45(2)
C(22)	−51(14)	5021(12)	1673(5)	57(3)
C(23)	−897(14)	5071(12)	1243(5)	61(3)
C(24)	−922(13)	4447(10)	774(5)	46(3)
C(25)	−40(13)	3782(11)	749(5)	51(3)
C(26)	777(13)	3814(11)	1195(5)	52(3)
C(211)	−1848(13)	4456(11)	308(5)	47(3)
C(212)	−2302(16)	5398(14)	297(6)	80(4)
C(213)	−3210(17)	5424(15)	−135(6)	85(5)
C(214)	−3597(16)	4482(13)	−549(6)	77(4)
C(215)	−3103(16)	3580(14)	−556(6)	80(4)
C(216)	−2242(14)	3534(12)	−128(5)	65(3)
N(31)	1130(10)	2593(9)	2266(4)	48(2)
C(32)	−246(13)	2026(11)	2161(4)	49(3)
C(33)	−940(14)	795(12)	2147(5)	57(3)
C(34)	−158(13)	150(11)	2259(5)	47(3)
C(35)	1322(13)	757(11)	2373(5)	52(3)
C(36)	1943(14)	1976(11)	2362(5)	54(3)
C(311)	−866(14)	−1148(12)	2260(5)	54(3)
C(312)	−2079(15)	−1857(13)	1924(5)	65(3)
C(313)	−2750(18)	−3100(15)	1920(7)	92(5)9
C(314)	−2176(17)	−3538(15)	2276(6)	83(4)
C(315)	−997(17)	−2858(14)	2607(6)	84(4)
C(316)	−281(16)	−1594(14)	2614(6)	77(4)
N(41)	3514(10)	4699(9)	3006(4)	47(2)
C(42)	3060(14)	4227(11)	3413(5)	57(3)
C(43)	3948(15)	4312(12)	3835(5)	64(3)
C(44)	5392(13)	4923(11)	3886(5)	50(3)
C(45)	5891(13)	5438(11)	3475(5)	52(3)
C(46)	4946(13)	5300(10)	3052(5)	48(3)
C(411)	6391(15)	5040(13)	4336(5)	63(3)
C(412)	6136(21)	4044(18)	4564(7)	109(6)
C(413)	7211(20)	4167(18)	5014(8)	114(6)
C(414)	8322(19)	5183(16)	5173(7)	95(5)
C(415)	8556(20)	6164(17)	4956(7)	103(5)
C(416)	7566(17)	6098(15)	4527(6)	82(4)
SG(4)	448(9)	9091(6)	673(3)	99(3)
SG(41)	1766(66)	9441(42)	723(18)	212(24)
OG(4)	855(16)	8809(13)	187(6)	140(5)
CG(41)	1198(21)	10627(18)	871(8)	117(6)
CG(42)	1331(23)	8642(20)	1143(8)	131(7)
SG(3)	4325(8)	424(6)	9355(3)	91(3)
SG(32)	3046(21)	257(16)	9164(7)	116(8)
OG(3)	4209(16)	781(13)	8852(6)	140(5)
CG(31)	3017(21)	−1114(18)	9229(7)	116(6)
CG(32)	3682(24)	1341(21)	9781(9)	148(6)
CG(11)	3768(24)	10892(20)	5925(8)	71(2)
CG(12)	3134(23)	11175(20)	6358(8)	71(2)
CG(13)	2103(23)	10221(20)	6499(8)	71(2)
CG(14)	1728(23)	9075(20)	6203(9)	71(2)
CG(15)	2203(23)	8716(20)	5817(9)	71(2)
CG(16)	3339(23)	9591(20)	5632(8)	71(2)
CG(17)	467(23)	8026(19)	6410(8)	71(2)
CG(7)	5385(23)	11923(23)	5784(11)	191(8)
CG(24)	7879(0)	9668(0)	5575(0)	191(8)
CG(25)	8728(0)	10897(0)	5681(0)	191(8)
CG(26)	8126(0)	11732(0)	5833(0)	191(8)
CG(21)	6676(0)	11336(0)	5879(0)	191(8)
CG(22)	5827(0)	10107(0)	5773(0)	191(8)
CG(23)	6428(0)	9272(0)	5621(0)	191(8)
CG(27)	8432(82)	8703(55)	5234(29)	191(8)

[a] Anisotropic atoms have thermal parameters of the form: $T = \{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^* + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*) \times 10^3\}$, with the following parameters. Ni(1): U_{11}, 43(1); U_{22}, 38(1); U_{33}, 42(1); U_{23}, 11(1); U_{13}, 11(1); U_{12}, 10(1). S(1): U_{11}, 101(3); U_{22}, 108(4); U_{33}, 55(2); U_{23}, 28(2); U_{13}, 32(2); U_{12}, 60(3). S(2): U_{11}, 96(3); U_{22}, 102(3); U_{33}, 72(3); U_{23}, 27(3); U_{13}, 36(2); U_{12}, 61(3).

angles [τ_1 τ_3 τ_5 τ_7] which yielded the minimum in the sum of the square of their differences. The result is shown in Fig. 3 which displays the torsion angles of the pyridines and those of their corresponding phenyl moieties. The torsion angles describing the pyridine moieties are remarkably similar, corresponding to the 'propeller' configuration found in the structures of the analogous compounds containing 4-vinyl, 4-ethyl and 4-methyl pyridines [4, 5, 8]. This corresponds to the ++++ configuration as described by Lipkowski [8]. However, since in our case the host complex is described by pairs of torsion angles, these can be summarized as:

I: ++, ++, ++, ++
II: ++, ++, ++, ++
III: ++, +−, ++, +−
IV: ++, ++, ++, ++

Packing of the α-form, compound **I**, is very similar to that of the α-form of the analogous 4-vinyl compound [4]. Packing of the host molecules in the clathrating forms, compounds **II**, **III** and **IV** leads to

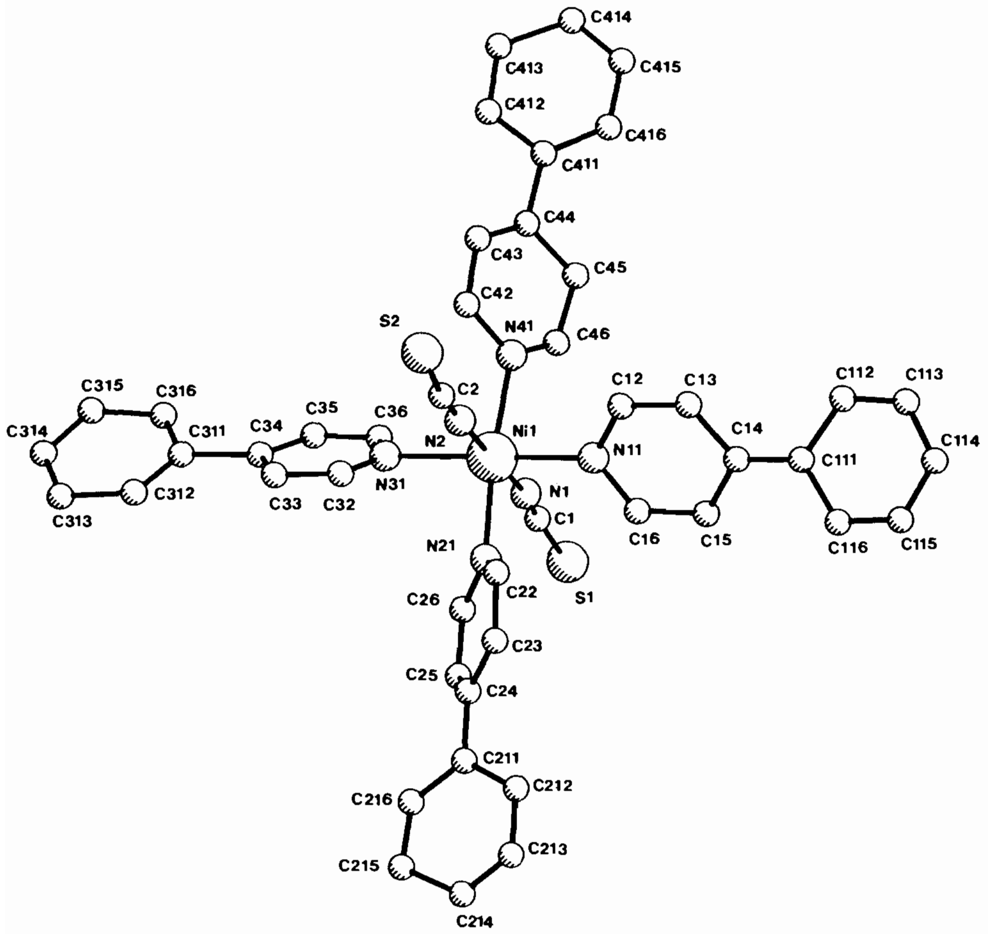

Fig. 2. Perspective view of an host molecule of **I** with atomic nomenclature.

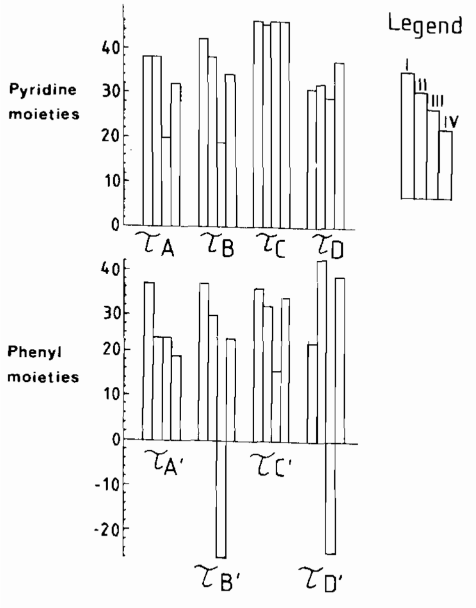

Fig. 3. Histograms of the pyridine and phenyl torsion angles.

the formation of a series of channels in which the guest molecules are located.

In **II**, the *o*-xylene molecules are situated in channels running alternately in the [101] and [10$\bar{1}$] directions in the planes of the diamond glides perpendicular to *b*. The packing is shown in Fig. 4, which displays the structure along [100], with the guest molecules of *o*-xylene shaded for clarity.

In **III**, the *m*-xylene molecules are situated in channels running parallel to *a* at $b=\frac{1}{2}$, $c=0$ and in the equivalent channel at $b=c=\frac{1}{2}$. Packing of the host molecules in this compound causes a considerable overlap of pyridine ligands when viewed along [010]. Close contacts between these ligands, on average 3.7 Å, causes distortion of the N(21)–Ni(1)–N(11) bond angle from the ideal 90° to 93.3°. This is shown in Fig. 5, which displays the packing of the structure viewed along [100], with the *m*-xylene guest molecules shaded.

The packing **IV** is shown in Figs. 6 and 7. The [100] projection of the structure, Fig. 6, displays the cross sections of the two non-equivalent channels running parallel to *a*. The projection is drawn omit-

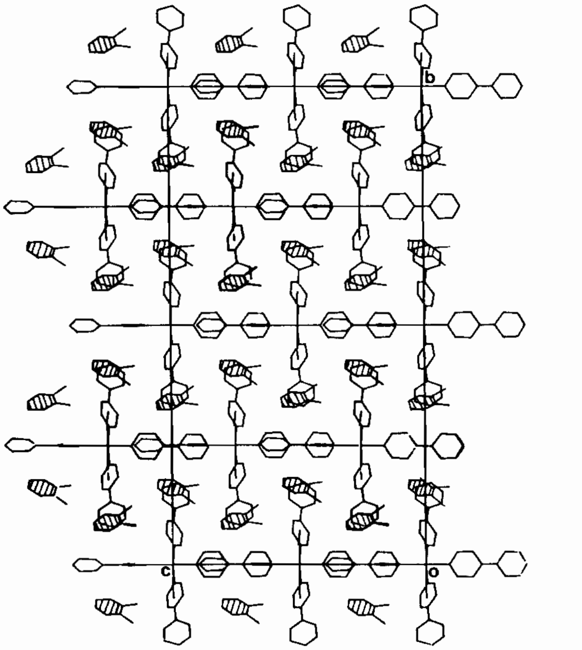

Fig. 4. Projection of structure **II** viewed along [100], with guest molecules shaded.

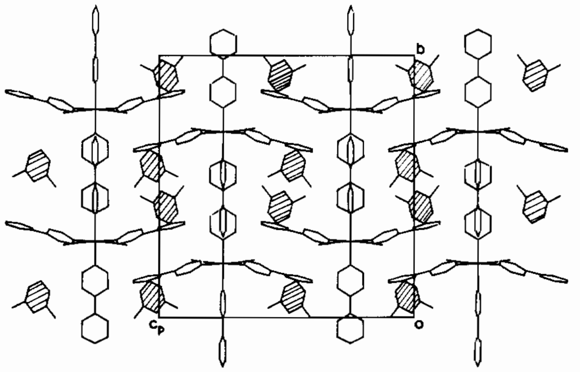

Fig. 5. Projection of structure **III** viewed along [100], with guest molecules shaded.

ting the guest molecules for clarity. The corresponding view along [010] is shown in Fig. 7 which shows the disordered DMSO molecules located in the channel at $b = 0$ and 1, while the disordered *p*-xylenes lie in the central channel at $b = 1/2$.

We note that this is the first Werner clathrate in which *p*-xylene has exhibited severe disorder. In all previous studies of similar structures we have noted disorder in *o*- and *m*-xylene which have invariably been required to lie at crystallographic centres of inversion while *p*-xylene has been satisfactorily located [4, 5, 8].

Supplementary Material

Detailed tables of bond lengths and angles are given as Supplementary Material, available from the authors on request.

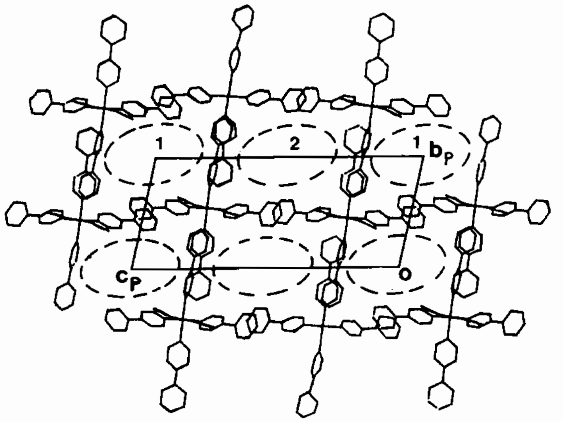

Fig. 6. Projection of structure **IV** viewed along [100]. The guest molecules are omitted and the extent of the channel is shown by broken lines.

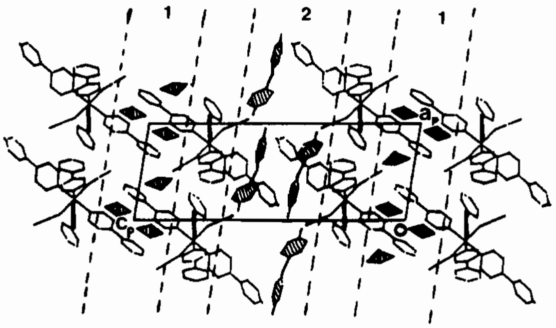

Fig. 7. Projection of structure **IV** viewed along [010], with the disordered DMSO and *p*-xylene guest molecules shaded.

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