Bis(isothiocyanato)tetrakis(4-methylpyridine)nickel(II)–*o*-Xylene (1:2)*

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Abstract. $C_{26}H_{28}N_6NiS_2 \cdot 2C_8H_{10}$, $M_r = 759.7$, monoclinic, $P2_1/c$, $a = 11.48$ (1), $b = 11.49$ (2), $c = 32.72$ (4) Å, $\beta = 96.6$ (2)°, $U = 4284$ Å^3, $Z = 4$, $D_x = 1.178$ Mg m^{-3}, $F(000) = 1608$, $\mu(Cu K\alpha) = 1.71$ mm^{-1}. The structure consists of discrete, propeller-shaped $Ni(4\text{-}MePy)_4(NCS)_2$ molecules and two symmetrically independent sets of *o*-xylene molecules one of which shows some positional disorder. The structure was refined to $R = 0.098$ for 1242 observed reflections with most atoms refined isotropically.

Introduction. $Ni(4\text{-}MePy)_4(NCS)_2$ on contact with xylene isomers produces clathrate-type compounds (Schaeffer, Dorsey, Skinner & Christian, 1957). The clathrates are usually of tetragonal symmetry with a 1:1 guest/host molar ratio (Lipkowski, Suwińska, Andreetti & Stadnicka, 1981), but *o*-xylene of an appropriate purity yields a different crystalline phase (Starzewski & Lipkowski, 1979) with a 2:1 guest/host molar ratio. Formation of this compound is '*ortho*-selective' instead of '*para*-selective' as is usually observed for samples of the above-mentioned tetragonal clathrates (Starzewski & Lipkowski, 1979). It thus seemed of interest to determine the structure of the title compound.

Crystals of a size suitable for X-ray analysis were produced by crystallization of the $Ni(4\text{-}MePy)_4(NCS)_2$ host complex from solutions in *o*-xylene: slow cooling of the solution saturated at 333 K gave large, deep-blue clathrate crystals. A crystal $0.35 \times 0.30 \times 0.25$ mm was mounted along **a**. To prevent deterioration in air (desorption of the guest component), it was mounted inside a Lindemann-glass capillary tube with a small amount of the mother liquor.

3009 independent reflections were measured up to $\theta = 35°$ on a Siemens AED computer-controlled three-circle diffractometer with filtered Cu $K\alpha$ radiation. The ω–2θ and five-points techniques (Hoppe, 1969) were used. 1242 reflections having $I \geq 2\sigma(I)$ were used in the structure analysis. Lorentz and polarization corrections were applied but no correction for absorption was made.

The structure was solved by direct methods with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). Subsequent electron-density calculations revealed the positions of all the non-H atoms of the host complex and of one guest molecule (*A*). Interpretation of the electron-density distribution over the other guest molecule (*B*) presented problems. Disorder has finally been assumed as the reason for that. The assumption that the *o*-xylene *B* occupies two different positions, B_1 and B_2, enabled the structure to be refined. The small number of observed reflections supports the concept of some disorder in the structure. In view of this, only a rather limited set of parameters was refined. Anisotropic thermal parameters were assigned only to the atoms of the $Ni(NCS)_2$ subunit. The *o*-xylene molecules were refined as rigid groups, molecules B_1 and B_2 with idealized geometry (regular hexagon for the aromatic ring), while the geometry of molecule *A* was refined in the final cycles. H atoms were placed in calculated positions. The final R was 0.098. The site-occupation factors (s.o.f.'s) for the two positions of guest molecule *B* refined to 0.62 for B_1 and 0.38 for B_2. The maximum residual electron density in the final difference map was 0.37 e Å^{-3}. The refinement calculations were performed with *SHELX* (Sheldrick, 1975).

Discussion. The final atomic parameters for the non-H atoms are listed in Table 1.† Bond lengths and selected bond angles within the host complex are shown in Fig. 1.

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*Clathrate Inclusion Compounds of Bis(isothiocyanato)tetrakis(4-methylpyridine)nickel(II). IV. Part III: Lipkowski, Sgarabotto & Andreetti (1982).

† Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36258 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* $(\times 10^4)$ *and thermal parameters* $(\times 10^3)$ *for the non-H atoms with e.s.d.'s in parentheses*

	x	y	z	U (Å^2)
Ni	−1441 (4)	6851 (4)	8757 (1)	*
N(1)	−1827 (20)	6962 (23)	8124 (8)	*
N(2)	−1100 (24)	6779 (23)	9385 (8)	*
N(3)	222 (19)	6131 (18)	8699 (7)	74 (7)
N(4)	−655 (19)	8545 (20)	8763 (7)	86 (8)
N(5)	−3086 (18)	7564 (18)	8828 (7)	74 (7)
N(6)	−2178 (20)	5097 (20)	8736 (7)	80 (7)
S(1)	−2420 (9)	6923 (9)	7281 (3)	*
S(2)	−1242 (10)	6637 (11)	10224 (3)	*
C(1)	−2080 (29)	6947 (27)	7784 (11)	*
C(2)	−1121 (29)	6688 (27)	9726 (11)	*
C(3)	1130 (26)	6248 (23)	8968 (9)	77 (9)
C(4)	2206 (29)	5795 (26)	8969 (10)	93 (10)
C(5)	2375 (27)	5004 (26)	8656 (9)	87 (10)
C(6)	1441 (26)	4852 (26)	8357 (10)	88 (10)
C(7)	387 (27)	5397 (25)	8380 (9)	90 (10)
C(8)	3561 (28)	4454 (31)	8626 (11)	133 (13)
C(9)	−5 (25)	8802 (29)	8445 (10)	92 (11)
C(10)	627 (26)	9864 (27)	8463 (10)	91 (10)
C(11)	566 (26)	10655 (28)	8790 (10)	95 (11)
C(12)	−61 (25)	10324 (29)	9104 (10)	98 (11)
C(13)	−721 (26)	9308 (28)	9085 (10)	93 (10)
C(14)	1284 (25)	11793 (27)	8804 (9)	106 (10)
C(15)	−3737 (24)	7229 (25)	9133 (9)	82 (10)
C(16)	−4847 (29)	7614 (27)	9175 (10)	99 (11)
C(17)	−5340 (26)	8443 (27)	8922 (9)	86 (10)
C(18)	−4731 (27)	8805 (27)	8605 (9)	91 (10)
C(19)	−3626 (26)	8381 (26)	8574 (9)	90 (10)
C(20)	−6585 (28)	8901 (31)	8940 (10)	135 (13)
C(21)	−1575 (30)	4319 (30)	8987 (10)	109 (11)
C(22)	−1986 (25)	3130 (31)	8944 (9)	92 (9)
C(23)	−2907 (26)	2906 (27)	8682 (9)	87 (10)
C(24)	−3581 (29)	3700 (28)	8427 (10)	105 (11)
C(25)	−3103 (25)	4855 (28)	8478 (9)	83 (10)
C(26)	−3386 (29)	1631 (28)	8634 (10)	135 (13)

Guest molecule A

E.s.d.'s $(\times 10^4)$ (9) (13) (3) (6)

	x	y	z	U
C(43)	2111	7454	−1	114
C(44)	1703	8563	−34	123
C(45)	2458	9501	60	109
C(46)	3591	9344	217	115
C(47)	4033	8178	258	107
C(48)	3251	7274	145	110
C(49)	5281	7925	429	163
C(50)	3797	6064	227	162

Guest molecule B

Position B_1, s.o.f. = 0·62

E.s.d.'s $(\times 10^4)$(16) (21) (6) (7)

	x	y	z	U
C(33)	4389	8220	2630	152
C(34)	4423	9413	2553	119
C(35)	3390	10017	2427	174
C(36)	2321	9425	2377	135
C(37)	2285	8232	2455	101
C(38)	3320	7629	2581	155
C(41)	1141	7599	2402	216
C(42)	3282	6351	2664	179

Table 1 (*cont.*)

	x	y	z	U (Å^2)
Position B_2, s.o.f. = 0·38				
E.s.d.'s $(\times 10^4)$(25)	(29)	(9)	(7)	
C(27)	1307	8746	2317	94
C(28)	630	7735	2295	187
C(29)	1152	6666	2405	132
C(30)	2352	6610	2537	98
C(31)	3028	7621	2558	134
C(32)	2506	8689	2448	126
C(39)	4313	7561	2699	143
C(40)	3234	9773	2471	156

* Anisotropic temperature factors with e.s.d.'s

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	116 (4)	52 (3)	77 (5)	2 (3)	26 (3)	−5 (4)
N(1)	111 (20)	54 (17)	55 (27)	−2 (22)	6 (18)	2 (16)
N(2)	153 (24)	33 (17)	77 (30)	9 (21)	14 (21)	7 (17)
S(1)	206 (11)	98 (8)	94 (9)	3 (7)	21 (7)	8 (8)
S(2)	216 (12)	209 (13)	81 (9)	−5 (8)	53 (7)	−15 (10)
C(1)	174 (33)	29 (20)	30 (34)	−10 (25)	5 (23)	2 (21)
C(2)	149 (29)	13 (20)	76 (37)	25 (24)	33 (27)	4 (18)
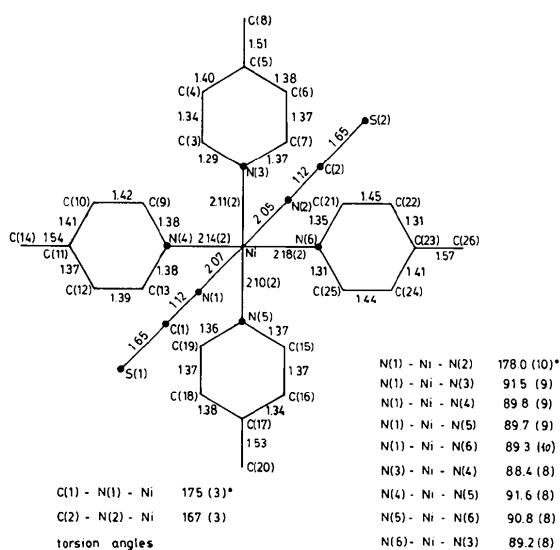
Fig. 1. A schematic diagram of the host Ni(4-MePy)$_4$(NCS)$_2$ molecule showing bond lengths (Å) and selected bond angles and torsion angles (°) with e.s.d.'s in parentheses (if omitted at a bond length, the e.s.d. is 0·03 Å).

The host Ni(4-MePy)$_4$(NCS)$_2$ molecule adopts a conformation very similar to that found in the 1-methylnaphthalene clathrate (Lipkowski, Sgarabotto & Andreetti, 1982).

The packing, shown in Fig. 2, is also similar to that in the 1-methylnaphthalene clathrate, and is of a layer type. The two guest molecules are in quite different situations. Molecules of A form layers composed of
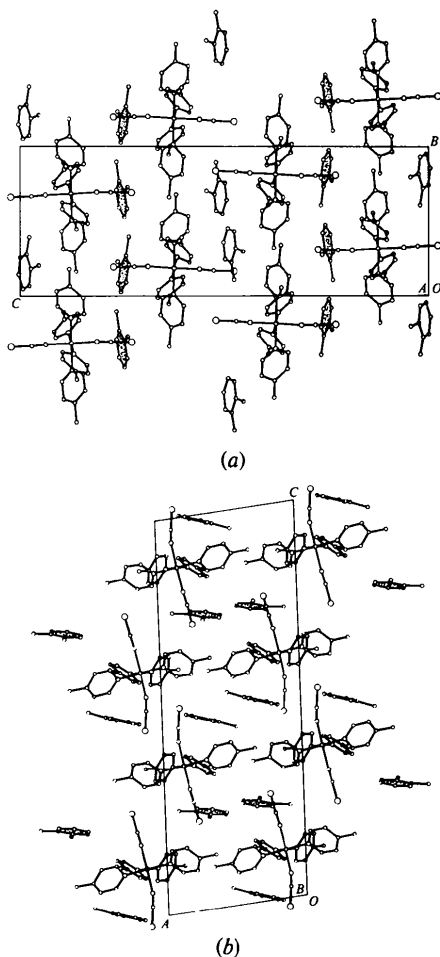
(a)

(b)

Fig. 2. The packing of the molecules viewed along (a) |100| and (b) [010]. The o-xylene molecules marked with dots are disordered (cf. text).

Fig. 3. Disordering mode for o-xylene guest molecule B viewed along [001] and |100|. Dashed lines are used for the B_2 position (s.o.f. = 0·38), solid lines for B_1 (s.o.f. = 0·62).

1982) is able to decrease its 'porosity' and absorb molecules smaller than 1-methylnaphthalene. Contraction of the host structure is not enough, however, to keep these smaller molecules ordered in the crystal. The difference in molar volume between the two clathrates is 31×10^{-6} m^3 mol^{-1}, i.e. $15\cdot5 \times 10^{-6}$ m^3 mol^{-1} per mole of the guest, significantly less than the difference between the molar volumes of liquid 1-methylnaphthalene and o-xylene ($142\cdot1 \times 10^{-6} - 120\cdot5 \times 10^{-6} = 21\cdot6 \times 10^{-6}$ m^3 mol^{-1}).

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centrosymmetrically related pairs of o-xylene molecules, at $z = 0$ and $\frac{1}{2}$. Layers at $z = \frac{1}{4}$ and $\frac{3}{4}$ consist of disordered guest molecules (for clarity just one position, B_1, is indicated in Fig. 2). As may be seen from Fig. 3 a superposition of B_1 and B_2 resembles quite well the molecular shape of 1-methylnaphthalene.

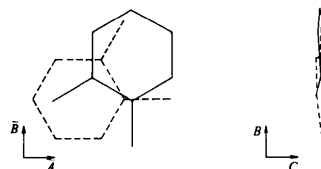The present results show that the 1-methylnaphthalene clathrate (Lipkowski, Sgarabotto & Andreetti,