

## Clathrate Inclusion Compounds of Bis(Isothiocyanato)tetrakis-(4-methylpyridine)nickel(II).

### I. Compounds with 2-Methyl- and 2-Bromonaphthalene as Guest Components

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#### Abstract

The structures of two isostructural  $[\text{Ni}(\text{C}_6\text{H}_7\text{N})_4(\text{NCS})_2] \cdot 2G$  clathrates, where  $G = 2$ -methyl- or 2-bromonaphthalene, were determined by X-ray diffraction and refined to  $R = 0.037$  and  $R = 0.045$  for 5577 and 2624 observed reflections of the 2-methyl- and 2-bromonaphthalene clathrates, respectively. Discrete, centrosymmetric  $\text{Ni}(\text{4-methylpyridine})_4(\text{NCS})_2$  molecules form layers of the host structure. The space between these layers is subdivided by the NCS groups of the host into centrosymmetric cavities, each being occupied by two guest molecules. An effect of intramolecular non-bonded interactions on the Ni–N coordination bonds was observed. [Crystal data: 2-methylnaphthalene clathrate:  $\text{C}_{48}\text{H}_{48}\text{N}_6\text{NiS}_2$ , triclinic,  $a = 11.309$  (12),  $b = 9.584$  (8),  $c = 11.656$  (14) Å,  $\alpha = 115.5$  (1),  $\beta = 82.0$  (1),  $\gamma = 108.7$  (1)°,  $Z = 1$ ; 2-bromonaphthalene clathrate:  $\text{C}_{46}\text{H}_{42}\text{Br}_2\text{N}_6\text{NiS}_2$ , triclinic,  $a = 11.31$  (1),  $b = 9.54$  (2),  $c = 11.76$  (3) Å,  $\alpha = 115.9$  (2),  $\beta = 81.7$  (1),  $\gamma = 109.6$  (1)°,  $Z = 1$ .]

#### Introduction

$\text{Ni}(\text{4-MePy})_4(\text{NCS})_2^*$  has received considerable attention because it is one of the most versatile formers of clathrates (Schaeffer, Dorsey, Skinner & Christian, 1957). Different crystal host structures of  $\text{Ni}(\text{4-MePy})_4(\text{NCS})_2$  can include various molecules as guest components. Most stable are clathrates of aromatic guests but also aliphatic compounds and even rare gases can be enclathrated (Allison & Barrer, 1969). A variety of crystalline structures has been found for the clathrates mentioned above (Casellato & Casu, 1969;

Lipkowski, Bylina, Duszczyk, Leśniak & Sybilka, 1974), only few of them being determined from X-ray diffraction studies. The non-clathrated  $\alpha$  phase of the host is monoclinic  $P2_1/c$  (Kerr & Williams, 1977), the  $p$ -terphenyl clathrate is triclinic  $P\bar{1}$  (Andreetti, Cavalca & Sgarabotto, 1970). The  $\beta$  phase, which exhibits zeolitic properties permitting guest desorption without collapse of the host lattice (Lipkowski & Majchrzak, 1975), is tetragonal  $I4_1/a$  (Andreetti, Bocelli & Sgarabotto, 1972; de Gil & Kerr, 1977). The present paper reports the structure determination of the 2-methylnaphthalene (abbreviated 2-MeN)<sup>†</sup> and 2-bromonaphthalene (2-BrN) inclusion compounds of  $\text{Ni}(\text{4-MePy})_4(\text{NCS})_2$ . Knowledge of the structures is pertinent to the interpretation of data on selective clathration and excitation energy transfer in these clathrates (Guarino, Occhiucci, Possagno & Bassanelli, 1976).

#### Experimental

Single crystals were synthesized according to the method of Kemula, Lipkowski & Sybilka (1974). Preliminary cell parameters and space-group information were obtained from Weissenberg photographs taken with filtered Cu  $K\alpha$  radiation. Crystals  $0.25 \times 0.35 \times 0.5$  mm (2-MeN) and  $0.10 \times 0.15 \times 0.3$  mm (2-BrN) were mounted along  $c$ . To prevent deterioration (desorption of the guest components) in air, the crystals with small amounts of the corresponding mother liquors were mounted inside Lindemann-glass capillaries.

Accurate cell parameters were determined from 21 reflections with  $\theta$  between 17 and 26° by least squares. Intensities, up to  $\theta = 31^\circ$  (2-MeN) and  $\theta = 26^\circ$  (2-BrN), were collected on a computer-controlled Siemens

\* 4-MePy = 4-methylpyridine ( $\text{MeC}_5\text{H}_4\text{N}$ ).

†  $\text{MeC}_{10}\text{H}_7$ .

AED diffractometer with filtered Mo  $K\alpha$  radiation. The  $\omega$ - $2\theta$  and five-points techniques (Hoppe, 1969) were used. 6920 (2-MeN) and 5402 (2-BrN) independent reflections were measured but 5577 (2-MeN) and 2624 (2-BrN) reflections having  $I \geq 2\sigma(I)$  were used in the analysis. Lorentz and polarization corrections were

applied, absorption was ignored. The main crystallographic data are given in Table 1. (Lattice constants for the *p*-terphenyl clathrate are also shown for comparison.)

The crystal structure of the 2-MeN clathrate was solved from a Patterson synthesis; *SHELX* was used (Sheldrick, 1975). First, the position for Ni was found; a subsequent electron density calculation revealed the positions of all the non-hydrogen atoms; *R* was 0.27. Then, the two pyridine rings were converted into regular hexagons; the same procedure was applied to the two rings of the naphthalene molecule; the distances Ni-N-C-S were fixed as 2.06, 1.17 and 1.61 Å respectively; 2.13 Å was assumed for the distance between Ni and the picoline N atoms. Preliminary refinement with the above geometrical constraints gave *R* = 0.20. After removal of the constraints, full-matrix least-squares refinement with isotropic thermal parameters reduced *R* to 0.14. Next, the refinement was extended to include anisotropic temperature factors and a variable site-occupation factor of the guest 2-MeN (*R* = 0.09). H atoms were found from a difference synthesis and included, with isotropic thermal parameters, in the final cycles. The final *R* was 0.037, the site-occupation factor of the guest 2-MeN being practically unity (0.997).

Table 1. *Crystallographic data*

Guest compound	2-MeN	2-BrN	
Formula	$\text{C}_{48}\text{H}_{48}\text{N}_6\text{NiS}_2$	$\text{C}_{46}\text{H}_{42}\text{Br}_2\text{N}_6\text{NiS}_2$	
$M_r$	822.6	952.4	
Space group	$P\bar{1}$	$P\bar{1}$	
<i>a</i>	11.309 (12) Å	11.31 (1) Å	10.73 (1) Å*
<i>b</i>	9.584 (8)	9.54 (2)	9.56 (1)
<i>c</i>	11.656 (14)	11.76 (3)	11.25 (1)
$\alpha$	115.5 (1)°	115.9 (2)°	117.8 (3)°
$\beta$	82.0 (1)	81.7 (1)	80.7 (3)
$\gamma$	108.7 (1)	109.6 (1)	96.7 (3)
<i>V</i>	1080 Å <sup>3</sup>	1074 Å <sup>3</sup>	
<i>Z</i>	1	1	
$D_c$	1.26 Mg m <sup>-3</sup>	1.47 Mg m <sup>-3</sup>	
<i>F</i> (000)	438	490	
$\mu$ (Mo $K\alpha$ )	0.54 mm <sup>-1</sup>	2.37 mm <sup>-1</sup>	

\* Data for the *p*-terphenyl clathrate. The given values correspond to the 001/010/ $\bar{1}$ 00 unit cell, with respect to the cell reported by Andreotti *et al.* (1970).

Table 2. *Final positional parameters* ( $\times 10^4$ ) *with e.s.d.'s in parentheses*

2-MeN clathrate				2-BrN clathrate			
Host	<i>x</i>	<i>y</i>	<i>z</i>	Host	<i>x</i>	<i>y</i>	<i>z</i>
Ni	0	0	5000	Ni	0	0	5000
N(1)	387 (1)	1868 (2)	4459 (1)	N(1)	405 (4)	1901 (5)	4508 (4)
N(2)	-731 (1)	-1663 (2)	3159 (1)	N(2)	-721 (4)	-1639 (5)	3160 (4)
N(3)	1875 (1)	-261 (1)	4403 (1)	N(3)	1884 (5)	-247 (6)	4392 (4)
S	1380 (1)	4267 (1)	3571 (1)	S	1346 (2)	4285 (2)	3608 (2)
C(1)	783 (1)	2862 (2)	4089 (1)	C(1)	778 (5)	2906 (6)	4148 (5)
C(2)	-1389 (2)	-1257 (2)	2544 (2)	C(2)	-1365 (6)	-1228 (8)	2568 (6)
C(3)	-1889 (2)	-2268 (3)	1363 (2)	C(3)	-1854 (6)	-2252 (9)	1369 (6)
C(4)	-1716 (2)	-3792 (2)	737 (2)	C(4)	-1685 (6)	-3772 (8)	729 (6)
C(5)	-1033 (2)	-4206 (2)	1369 (2)	C(5)	-1012 (6)	-4189 (7)	1339 (6)
C(6)	-576 (2)	-3135 (2)	2569 (2)	C(6)	-562 (6)	-3114 (7)	2540 (6)
C(7)	-2247 (3)	-4937 (4)	-555 (2)	C(7)	-2235 (8)	-4929 (10)	-576 (8)
C(8)	2180 (1)	-1553 (2)	4282 (2)	C(8)	2195 (5)	-1527 (6)	4303 (6)
C(9)	3309 (2)	-1831 (2)	3812 (2)	C(9)	3321 (6)	-1791 (7)	3826 (7)
C(10)	4201 (1)	-732 (2)	3440 (2)	C(10)	4196 (5)	-728 (7)	3411 (7)
C(11)	3901 (2)	619 (3)	3593 (2)	C(11)	3885 (6)	599 (8)	3517 (7)
C(12)	2756 (2)	815 (2)	4071 (2)	C(12)	2740 (5)	780 (8)	3997 (6)
C(13)	5425 (2)	-1011 (4)	2889 (3)	C(13)	5415 (7)	-1019 (10)	2859 (7)
2-MeN				2-BrN			
C(14)	-3260 (2)	1389 (3)	234 (2)	C(14)	-3292 (6)	1408 (8)	280 (6)
C(15)	-2186 (2)	1070 (2)	322 (2)	C(15)	-2261 (6)	1085 (8)	390 (6)
C(16)	-1587 (2)	1831 (2)	1499 (2)	C(16)	-1593 (6)	1867 (8)	1539 (6)
C(17)	-2036 (2)	2882 (2)	2544 (2)	C(17)	-2045 (6)	2953 (8)	2571 (6)
C(18)	-3579 (2)	4408 (3)	3497 (2)	C(18)	-3543 (7)	4505 (9)	3518 (7)
C(19)	-4615 (2)	4769 (3)	3365 (2)	C(19)	-4594 (8)	4859 (10)	3408 (8)
C(20)	-5243 (2)	3990 (3)	2220 (2)	C(20)	-5237 (7)	4079 (10)	2284 (8)
C(21)	-4836 (2)	2880 (3)	1201 (2)	C(21)	-4823 (7)	2923 (9)	1250 (7)
C(22)	-3753 (2)	2487 (2)	1283 (2)	C(22)	-3765 (5)	2539 (8)	1327 (6)
C(23)	-3126 (2)	3252 (2)	2454 (2)	C(23)	-3119 (6)	3332 (7)	2495 (6)
C(24)	-1635 (3)	-11 (4)	-814 (3)	Br	-1655 (1)	-434 (1)	-1006 (1)

The coordinates of the non-hydrogen atoms of the 2-MeN clathrate (except for the naphthalene methyl group) were used as a first approximation in solving the 2-BrN crystal structure. An electron density calculation revealed the position of the Br atom. At this stage  $R$  was 0.18 and the structure was refined with isotropic thermal parameters to  $R = 0.109$ . Subsequent full-matrix least-squares refinement, with anisotropic thermal parameters of non-hydrogen atoms, isotropic H atoms being located geometrically (1.08 Å) and riding on their C atoms, reduced  $R$  to the final 0.045. The refined s.o.f. value of guest 2-BrN was 0.967.

The final atomic parameters of both structures are listed in Table 2.\*

## Results and discussion

### Molecular structure

The bond lengths and angles in the host Ni(4-MePy)<sub>4</sub>(NCS)<sub>2</sub> are given in Table 3. Least-squares planes through various groups of atoms in both structures are presented in Table 4.

The conformation of the Ni(4-MePy)<sub>4</sub>(NCS)<sub>2</sub> host is essentially the same in both clathrates and is similar to that found in the *p*-terphenyl clathrate (Andreotti, Cavalca & Sgarabotto, 1970). The overall shape of the molecule is depicted in an ORTEP projection (Fig. 1). The Ni has distorted octahedral coordination of the six N atoms of the two isothiocyanate and four pyridine ligands. The Ni—N distances show significant differences not only between isothiocyanate and 4-MePy groups, but also between the two symmetrically independent 4-MePy groups. This last non-equivalency is, in our opinion, caused by intramolecular repulsion between thiocyanate groups and N(3), N(3)' 4-MePy groups. From the N(1)—Ni—N(3) plane these two symmetrically located N(3) and N(3)' 4-MePy groups are twisted by 9° (2-MeN) and 4° (2-BrN). As may be seen from Table 5, the intramolecular non-bonded contacts H(8)···N(1), C(8)···N(1) and H(8)···S are the shortest and differ significantly from the corresponding sums of van der Waals radii. On the other hand, no significant shortening of intermolecular distances compared to sums of van der Waals radii is observed. Moreover, the bond distances and angles within the two symmetrically independent 4-MePy ligands are exactly equal to each other. Thus the non-bonded interactions mentioned above seem to be the only explanation for the lengthening of the Ni—N(3) distance. The lengthening

Table 3. Bond distances (Å), angles (°) and torsion angles (°) with e.s.d.'s in parentheses in the Ni(4-MePy)<sub>4</sub>(NCS)<sub>2</sub> host

	2-MeN clathrate	2-BrN clathrate
In square brackets are given the values corrected for libration.		
Ni—N(1)	2.046 (2)	2.029 (7)
Ni—N(2)	2.129 (3)	2.119 (8)
Ni—N(3)	2.196 (2)	2.203 (6)
N(1)—C(1)	1.149 (2)	1.144 (8)
C(1)—S	1.624 (2)	1.610 (7)
N(2)—C(2)	1.339 (3) [1.349]	1.321 (10) [1.332]
N(2)—C(6)	1.336 (2) [1.346]	1.334 (8) [1.345]
C(2)—C(3)	1.368 (3) [1.373]	1.381 (9) [1.387]
C(3)—C(4)	1.389 (3) [1.400]	1.377 (11) [1.388]
C(4)—C(5)	1.380 (4) [1.390]	1.364 (12) [1.375]
C(4)—C(7)	1.496 (3) [1.502]	1.515 (11) [1.521]
C(5)—C(6)	1.379 (3) [1.385]	1.377 (9) [1.383]
N(3)—C(8)	1.335 (2) [1.347]	1.338 (10) [1.350]
N(3)—C(12)	1.335 (2) [1.348]	1.320 (9) [1.332]
C(8)—C(9)	1.378 (3) [1.383]	1.373 (9) [1.377]
C(9)—C(10)	1.380 (3) [1.394]	1.366 (10) [1.377]
C(10)—C(11)	1.375 (4) [1.388]	1.374 (12) [1.387]
C(10)—C(13)	1.497 (3) [1.503]	1.496 (10) [1.501]
C(11)—C(12)	1.374 (3) [1.379]	1.370 (9) [1.375]
N(1)—Ni—N(2)	90.0 (2)	89.7 (5)
N(1)—Ni—N(3)	90.3 (2)	90.2 (5)
N(2)—Ni—N(3)	91.3 (2)	90.7 (5)
N(1)—C(1)—S	178.5 (2)	177.6 (13)
Ni—N(1)—C(1)	169.0 (4)	170.3 (12)
Ni—N(2)—C(2)	120.1 (4)	120.4 (10)
Ni—N(2)—C(6)	123.0 (4)	123.1 (10)
Ni—N(3)—C(8)	121.9 (3)	121.7 (8)
Ni—N(3)—C(12)	122.1 (4)	122.3 (8)
C(2)—C(3)—C(4)	120.2 (4)	120.8 (13)
C(2)—N(2)—C(6)	117.0 (4)	116.5 (13)
N(2)—C(2)—C(3)	123.1 (5)	122.6 (13)
C(3)—C(4)—C(5)	116.7 (5)	116.5 (14)
C(3)—C(4)—C(7)	122.0 (4)	121.7 (13)
C(4)—C(5)—C(6)	120.0 (5)	119.7 (14)
N(2)—C(6)—C(5)	123.1 (4)	123.9 (12)
C(5)—C(4)—C(7)	121.4 (5)	121.8 (15)
C(8)—N(3)—C(12)	115.9 (4)	115.7 (12)
C(8)—C(9)—C(10)	119.8 (4)	120.6 (11)
C(9)—C(10)—C(11)	116.5 (4)	116.3 (13)
C(9)—C(8)—N(3)	123.8 (4)	123.2 (12)
C(9)—C(10)—C(13)	121.5 (5)	121.3 (12)
C(10)—C(11)—C(12)	120.4 (5)	120.0 (12)
C(11)—C(10)—C(13)	122.0 (5)	122.4 (14)
C(11)—C(12)—N(3)	123.5 (4)	124.2 (11)
N(1)—Ni—N(2)—C(2)	38 (1)	38 (2)
N(1)—Ni—N(2)—C(6)	-143 (1)	-142 (2)
N(1)—Ni—N(3)—C(8)	167 (1)	170 (2)
N(1)—Ni—N(3)—C(12)	-9 (1)	-4 (3)

ing of Ni—N coordination bonds should influence the visible spectrum of the host complex, *i.e.* there should be a shift toward lower frequencies with respect to the visible spectrum of  $\alpha$ -Ni(4-MePy)<sub>4</sub>(NCS)<sub>2</sub>, in which the four N atoms of the 4-MePy ligands are at almost the same (2.128 Å) distance from Ni (Kerr & Williams, 1977). Such a spectral effect has recently been reported by Guarino, Occhiucci, Possagno & Bassanelli (1977).

\* Lists of structure factors, thermal parameters, H atom positional parameters and details of the rigid-body-motion analysis have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34785 (56 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The shift of the  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  band, when measured on samples of the 2-BrN or *p*-terphenyl clathrates, is  $-60 \text{ cm}^{-1}$ . Bond lengths and angles of the guest 2-MeN and 2-BrN molecules are given in Fig. 2. Deviations of atoms from the corresponding least-squares molecular planes of 2-MeN and 2-BrN may be found in Table 4.

Table 4. Some least-squares planes and atomic deviations (Å)

2-MeN clathrate

(a) N(2) 4-methylpyridine molecular plane

$$7.7460X + 3.3394Y - 6.0899Z = -3.0475$$

N(2)	0.002 (2)	C(5)	0.009 (2)
C(2)	-0.003 (2)	C(6)	-0.010 (2)
C(3)	-0.003 (2)	C(7)	-0.004 (3)
C(4)	0.003 (2)	Ni*	0.003

(b) N(3) 4-methylpyridine molecular plane

$$4.1561X - 0.1335Y + 9.7913Z = 5.1168$$

N(3)	-0.023 (2)	C(11)	0.014 (2)
C(8)	0.003 (2)	C(12)	0.004 (2)
C(9)	0.015 (2)	C(13)	-0.020 (3)
C(10)	0.007 (2)	Ni*	-0.221

(c) 2-MeN molecular plane†

$$3.1170X + 7.5968Y - 6.5232Z = 3.0442$$

C(14)	-0.041 (2)	C(20)	0.022 (2)
C(15)	-0.006 (2)	C(21)	-0.030 (2)
C(16)	-0.009 (2)	C(22)	-0.045 (2)
C(17)	-0.032 (2)	C(23)	-0.032 (2)
C(18)	0.025 (3)	C(24)	0.086 (3)
C(19)	0.062 (2)		

Dihedral angles

$$(a)-(c) = 32 (1)^\circ$$

$$(b)-(c) = 91 (1)^\circ$$

2-BrN clathrate

(a) N(2) 4-methylpyridine molecular plane

$$7.6567X + 3.3877Y - 6.0669Z = -3.0187$$

N(2)	-0.006 (6)	C(5)	0.012 (6)
C(2)	-0.004 (6)	C(6)	-0.008 (6)
C(3)	0.006 (6)	C(7)	-0.013 (10)
C(4)	0.008 (6)	Ni*	-0.015 (6)

(b) N(3) 4-methylpyridine molecular plane

$$4.1826X + 0.2594Y + 9.5287Z = 4.9785$$

N(3)	-0.012 (5)	C(11)	0.013 (6)
C(8)	0.000 (6)	C(12)	-0.004 (6)
C(9)	0.010 (6)	C(13)	-0.016 (10)
C(10)	0.008 (6)	Ni*	-0.214

(c) 2-BrN molecular plane†

$$3.1328X + 7.4073Y - 6.8265Z = 2.9467$$

C(14)	0.007 (6)	C(20)	0.008 (6)
C(15)	0.015 (6)	C(21)	-0.013 (6)
C(16)	0.019 (6)	C(22)	-0.019 (6)
C(17)	-0.022 (6)	C(23)	-0.026 (6)
C(18)	0.012 (6)	Br*	0.033 (1)
C(19)	0.020 (6)		

Dihedral angles

$$(a)-(c) = 30 (2)^\circ$$

$$(b)-(c) = 89 (2)^\circ$$

\* Atoms not included in the least-squares calculation.

† Molecule at  $1+x, y, z$ .

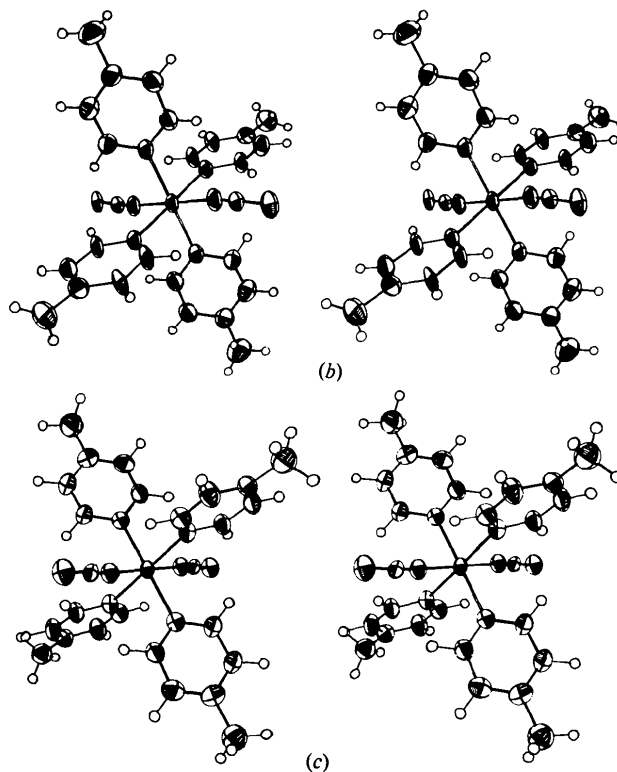
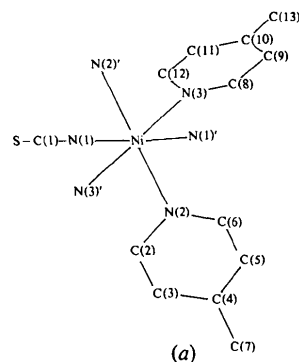


Fig. 1. The  $\text{Ni}(\text{4-MePy})_4(\text{NCS})_2$  host molecule: (a) atom numbering, and ORTEP (Johnson, 1965) stereoviews of the host as found in the (b) 2-MeN clathrate, (c) 2-BrN clathrate. Ellipsoids of 50% probability are used for non-hydrogen atoms; the H atoms are indicated by spheres of 0.1 Å radii.

### Thermal motion

The thermal motion of the 4-MePy ligands and the guest molecules of 2-MeN or 2-BrN has been analysed in terms of the rigid-body vibrations of translation (T) and libration (L), taking into account the correlation tensors (Schomaker & Trueblood, 1968). Corrections to bond lengths between atoms in the rigid bodies are included in Table 3 and Fig. 2. The most significant results of the thermal-motion analysis are listed in Table 6.\* The librational motion of the 4-MePy ligands

\* See deposition footnote.

Table 5. *Van der Waals closest contacts* (Å)

The number of an H atom is the same as that of the C atom to which it is attached.

Intramolecular within the host complex

	2-MeN clathrate	2-BrN clathrate	$r_1 + r_2^*$
N(1)···H(8)	2.359 (24)	2.381	2.70
N(1)···C(8)	3.051 (4)	3.044 (9)	3.20
N(1)···H(6)	2.663 (24)	2.690	2.70
N(1)···C(6)	3.153 (4)	3.155 (13)	3.20
C(1)···H(8)	2.867 (23)	2.792	2.90
N(3)···C(2)	3.255 (4)	3.265 (13)	3.20
C(8)···H(2)	3.039 (23)	2.937	2.90

Intermolecular

Host—host

S···C(8)	3.547 (4)	3.514 (12)	3.55
S···C(9)	3.586 (5)	3.575 (11)	3.55
S···H(8)	2.914 (28)	2.798	3.05
S···H(9)	2.998 (27)	2.964	3.05

Host—guest

H(5)···C(16)	2.969 (33)	2.897	2.90
H(5)···C(17)	2.991 (31)	2.986	2.90
H(11)···C(18)	2.953 (26)	2.876	2.90
H(11)···C(23)	3.038 (26)	2.880	2.90
S···H(18)	3.047 (28)	2.979	3.05
C(5)···C(23)	3.355 (5)	3.348 (11)	3.40

Guest—guest

H(19)···C(19)	2.979 (38)	—	2.90
H(19)···C(18)	3.008 (32)	3.040	2.90

\* Sum of van der Waals radii.

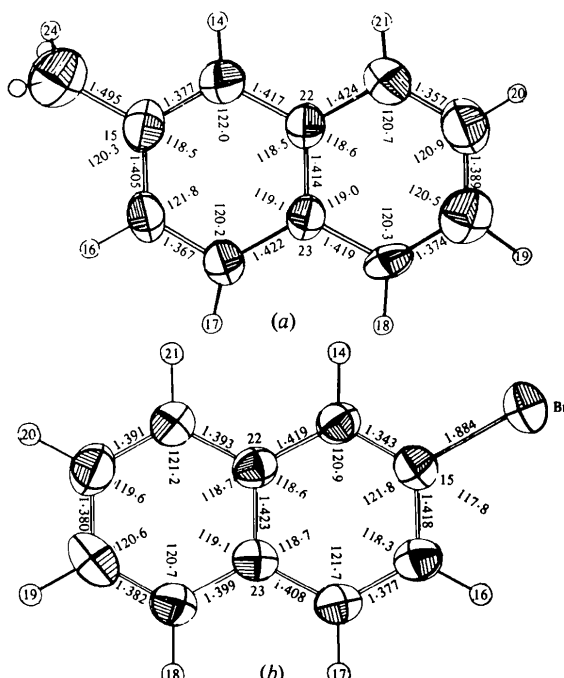


Fig. 2. An ORTEP plot of (a) 2-MeN and (b) 2-BrN molecules showing bond distances (Å) (corrected for libration) and angles (°). Ellipsoids of 50% probability are used for C and Br atoms; H atoms are represented by circles of 0.1 Å radii. Numbers inside the circles show the numbering of the C and H atoms.

is highly anisotropic: as expected, the principal axes of libration are nearly coincident with the corresponding Ni—N bond directions. The principal axes of translation of the guest 2-MeN and 2-BrN molecules are directed similarly in the two structures and seem to be defined mainly by geometrical relations between cage and guest molecules, which are similar in the two structures. Such an analogy does not, of course, appear when the principal axes of libration of the 2-MeN and 2-BrN molecules are compared, because of the presence of the heavy Br atom in 2-BrN.

### Packing

An illustration of the packing, which is essentially the same in the two clathrates, is given in projections along [100] and [010] (Fig. 3). The structure consists of discrete, centrosymmetric  $\text{Ni}(4\text{-MePy})_4(\text{NCS})_2$  and asymmetric guest molecules, the latter occupying voids between (011) close-packed layers of the host. Void space between these layers is subdivided into cavities by means of isothiocyanate groups. The cavities have centres of symmetry, each of the cavities being occupied by two symmetrically located 2-BrN or 2-

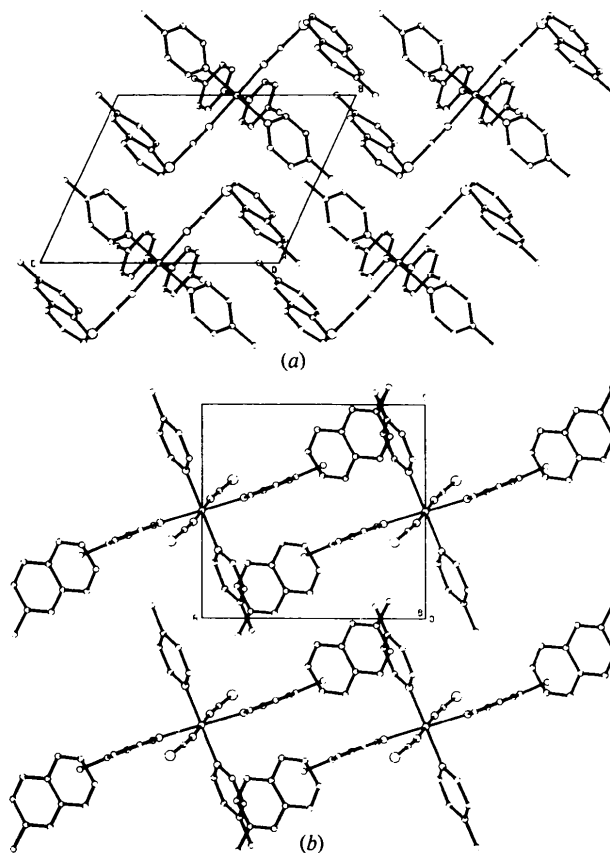


Fig. 3. The packing of the molecules viewed along (a) [100] and (b) [010].

Table 6. Selected results of rigid-body analysis of thermal motion

		2-MeN clathrate			2-BrN clathrate			
R.m.s. amplitudes†		Direction cosines‡ × 10 <sup>4</sup>			R.m.s. amplitudes†	Direction cosines‡ × 10 <sup>4</sup>		
N(2) 4-methylpyridines								
L	7.1°	-3495	-4935	-7964	7.6°	-3108	-5226	-7939
	4.3	1099	-8658	4883	4.7	6624	-7181	2134
	2.9	9305	-831	-3568	2.1	6816	4596	-5694
T	0.20 Å	6538	1588	7398	0.21 Å	6318	2380	7377
	0.18	-3779	9156	1374	0.18	-4857	8632	1375
	0.15	-6556	-3694	6586	0.13	-6041	-4452	6610
$\Delta U_{\text{r.m.s.}} = \langle (U_{\text{obs}} - U_{\text{calc}})^2 \rangle^{1/2} \text{ \AA}^2$							0.0027	
$\sigma_{\text{r.m.s.}}(U_{\text{obs}}) \text{ \AA}^2$							0.0031	
N(3) 4-methylpyridines								
L	8.4°	9134	-3906	-1143	8.2°	9116	-3854	-1429
	3.9	-2958	-8300	4729	4.3	-983	-5420	8346
	2.6	-2796	-3982	-8737	1.2	-3991	-7468	-5320
T	0.19 Å	4536	-1345	8810	0.19 Å	9611	-2760	62
	0.17	8745	-1236	-4691	0.18	-83	-67	9999
	0.18	1719	9832	616	0.15	-2760	-9611	-88
$\Delta U_{\text{r.m.s.}} = \langle (U_{\text{obs}} - U_{\text{calc}})^2 \rangle^{1/2} \text{ \AA}^2$							0.0030	
$\sigma_{\text{r.m.s.}}(U_{\text{obs}}) \text{ \AA}^2$							0.0029	
Guest molecules								
L	5.0°	6227	-7526	-2140	5.4°	4831	-8683	-1124
	3.6	-1598	-3901	9068	3.3	5606	2081	8015
	3.1	7660	5305	3632	2.7	6726	4502	-5873
T	0.21 Å	8141	-5806	-99	0.20 Å	7754	-6295	507
	0.20	2415	3231	9150	0.18	2654	3976	8783
	0.18	-5281	-7473	4033	0.16	-5731	6676	4753
$\Delta U_{\text{r.m.s.}} = \langle (U_{\text{obs}} - U_{\text{calc}})^2 \rangle^{1/2} \text{ \AA}^2$							0.0035	
$\sigma_{\text{r.m.s.}}(U_{\text{obs}}) \text{ \AA}^2$							0.0034	

† The mean e.s.d.'s of the r.m.s. amplitudes are:

	2-MeN clathrate	2-BrN clathrate
Libration	7%	26%
Translation	3%	11%

‡ The direction cosines are given in the orthogonalized coordinate system:  $X_0$  is parallel to  $x^*$ ,  $Y_0$  is parallel to  $z \times x^*$ ,  $Z_0$  is parallel to  $z$ .

MeN molecules. So, 2:1 is the maximum value for guest/host molar ratio. This value is almost achieved in the clathrates studied in the present work (1.99, 2-MeN; 1.93, 2-BrN).

Molecular planes of guest naphthalene rings and host 4-MePy ligands are not parallel (Table 4). Thus, the hypothesis of charge-transfer guest to host bonding in the  $\gamma$ -Ni(4-MePy)<sub>4</sub>(NCS)<sub>2</sub> clathrates having 2:1 guest/host molar ratios (Casellato & Casu, 1969) is not confirmed by the present study. Neither shortening of intermolecular contacts nor coplanarity of guest and host aromatic rings is observed.

If the centrosymmetric cavity is occupied by one molecule, it must adopt a centrosymmetric conformation as has been found in the *p*-terphenyl clathrate (Andreotti, Cavalca & Sgarabotto, 1970). The structure of the host is essentially the same in the 2-MeN, 2-BrN and *p*-terphenyl clathrates. Substitution of one

centrosymmetric *p*-terphenyl molecule by two centrosymmetrically located (in one cavity) 2-MeN or 2-BrN molecules leads to host lattice dilatation of approximately 60 Å<sup>3</sup> per unit cell. As is seen from the comparison given in Table 1 the dilatation is the result of a lengthening of about 0.5 Å in *a* and *c*.

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## Bis(oxamide oximato)platinum(II)— $\frac{1}{3}$ Sodium Acetate— $\frac{1}{3}$ Sodium Chloride—2-Water

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### Abstract

$C_4H_{10}N_8O_4Pt \cdot \frac{1}{3}C_2H_3NaO_2 \cdot \frac{1}{3}NaCl \cdot 2H_2O$ ,  $M_r = 512.17$ , crystallizes in space group  $P\bar{1}$ , with  $a = 10.032$  (3),  $b = 10.482$  (5),  $c = 12.020$  (5) Å,  $\alpha = 116.16$  (3),  $\beta = 85.32$  (2),  $\gamma = 103.13$  (2)°,  $V = 1105$  Å<sup>3</sup>,  $Z = 3$ ,  $d_c = 2.31$  Mg m<sup>-3</sup>. The final  $R = 0.054$  for 3557 reflections. The Pt complex units form stacks of triads along  $a$ , with Pt–Pt separations of 3.280 Å within a triad and 3.560 Å between triads. The complex molecules within a triad are linked by Pt–Pt interactions and by intermolecular H bridges between oxime O atoms.

### Introduction

The structural variability of transition-metal complexes of oxamide oxime (diaminoglyoxime, oaoH<sub>2</sub>) is presently being investigated (Bekaroglu, Sarisaban, Koray & Ziegler, 1977; Bekaroglu, Sarisaban, Koray, Nuber, Weidenhammer, Weiss & Ziegler, 1978). In the search for new materials with highly anisotropic physical properties we are interested in the oaoH complexes of the Ni triad (Endres, 1978, 1979*a,b*), for the  $\alpha,\beta$ -dione dioximato complexes of these metals are known to crystallize in stacked structures (Endres, Keller, Lehmann, Poveda, Rupp & van de Sand, 1977).

### Experimental

A solution of 415 mg K<sub>2</sub>[PtCl<sub>4</sub>] and 2 g NH<sub>4</sub>Cl in 100 ml H<sub>2</sub>O was added dropwise to a refluxing solution of 260 mg oxamide oxime (Ephraim, 1889), kept 1 h under reflux and allowed to cool to room temperature. Dark-red crystals and a greenish-black amorphous body were filtered off. The mother liquor was buffered with a saturated Na acetate solution to pH 7, and another crop of red crystals were filtered off. These products are still under investigation. The filtrate was evaporated on a sand bath to about 15 ml and allowed to cool slowly. Large colourless crystals of the buffer substances and a small amount of red columnar crystals of the title compound precipitated and were collected by filtration. When the buffer substances were removed by washing with H<sub>2</sub>O, the red crystals were attacked, too, and changed their habit. Hence analytical data are not available.

A crystal 0.18 × 0.05 × 0.06 mm was selected for the structure determination. Photographs (Cu  $K\alpha$  radiation) showed the crystal to be triclinic. A rotation photograph exhibited a pattern with each third layer line strong, characteristic for a stacked structure with metal–metal separations roughly one third of the cell length. Lattice constants were calculated by least squares (Berdiesinski & Nuber, 1966) from the diffrac-