

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

III.* Bis(isothiocyanato)tetrakis(4-methylpyridine)nickel(II)–1-Methylnaphthalene (1 : 2)†

BY JANUSZ LIPKOWSKI

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warszawa, Poland

AND PAOLO SGARABOTTO AND GIOVANNI D. ANDRETTI

Centro di Studio per la Strutturistica Diffraattometrica del Consiglio Nazionale delle Ricerche, via M. d'Azeglio 85, 43-100 Parma, Italy

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Abstract

The structure of $\text{Ni}(\text{C}_6\text{H}_7\text{N})_4(\text{NCS})_2 \cdot 2(1\text{-CH}_3\text{C}_{10}\text{H}_7)$ was determined by X-ray diffraction and refined to $R = 0.069$ for 5351 observed reflections. Discrete, asymmetric $\text{Ni}(4\text{-methylpyridine})_4(\text{NCS})_2$ molecules form layers of the host structure. The NCS groups are nearly perpendicular to these layers and subdivide the inter-layer space into a cage-like structure. There are two symmetrically independent guest molecules per molecule of the host complex. Crystal data: $\text{C}_{26}\text{H}_{28}\text{N}_6\text{NiS}_2 \cdot 2\text{C}_{11}\text{H}_{10}$, $M_r = 831.8$, is monoclinic, space group $P2_1/c$, with $a = 11.528(12)$, $b = 11.890(6)$, $c = 32.852(12)$ Å, $\beta = 94.28(6)^\circ$, $V = 4490$ Å³, $Z = 4$, $D_c = 1.230$ Mg m⁻³, $F(000) = 1752$, $\mu(\text{Cu K}\alpha) = 1.67$ mm⁻¹.

Introduction

$\text{Ni}(4\text{-MePy})_4(\text{NCS})_2$ ‡ when kept in contact with methanolic solutions of mixtures of 1- and 2-methylnaphthalene (1- and 2-MeN) forms a clathrate-type solid which is enriched with the 1-isomer rather than the 2-isomer (Schaeffer, Dorsey, Skinner & Christian, 1957). Lipkowski, Bylina, Duszczuk, Leśniak & Sybilska (1974) have found that at least two different crystalline products form in the above process: the 2-MeN and 1-MeN clathrates, the latter being less soluble than the former. In Part I of this study (Lipkowski, Sgarabotto & Andreotti, 1980) we reported the structures of the 2-MeN and 2-BrN clathrates. The present paper reports the crystal structure of the more stable 1-MeN clathrate. Knowledge of this

structure is necessary for the interpretation of data not only on selective clathration but also on guest–host interaction in the $\text{Ni}(4\text{-MePy})_4(\text{NCS})_2$ clathrates (Guarino, Occhiucci, Possagno & Bassanelli, 1977).

Experimental

Single crystals were synthesized as described by Kemula, Lipkowski & Sybilska (1974). When the crystals were removed from solution, they dried with significant loss of the guest component (1-MeN) and deterioration of the crystal structure. To avoid this, the crystals, together with small amounts of mother liquor, were mounted inside Lindemann-glass capillaries.

A crystal $0.6 \times 0.3 \times 0.2$ mm was mounted along *a*. Space group and preliminary cell parameters were determined from Weissenberg photographs. Accurate cell parameters were determined from 15 reflections with θ between 19 and 41° by least squares. Intensities up to $\theta = 70^\circ$ were collected on a computer-controlled Siemens AED diffractometer with filtered Cu *K* α radiation. The ω - 2θ and five-points techniques (Hoppe, 1969) were used. 7748 unique reflections were measured. Of these, 5351 having $I \geq 2\sigma(I)$ were classified as observed and used in the analysis. Lorentz and polarization corrections were applied but absorption was ignored.

The structure was solved from three-dimensional Patterson and electron-density syntheses, and refined by blocked full-matrix least squares using *SHELX* (Sheldrick, 1975). H atoms were placed in calculated positions ($\text{C-H} = 1.08$ Å) 'riding' on their C atoms. Anisotropic thermal parameters were refined for all non-H atoms except for the methyl C atoms. Site-occupation factors for the two independent 1-MeN molecules refined to 0.965 (5) and 0.999 (5) for molecules *A* and *B* respectively. The final $R = 0.069$

* Part II: Lipkowski, Suwińska, Andreotti & Stadnicka (1981).

† Preliminary communication: Lipkowski, Andreotti & Sgarabotto [*Acta Cryst.* (1978), **A34**, S145].

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

Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Hamilton, 1959) with e.s.d.'s in parentheses

| | x | y | z | B_{eq} (\AA^2) |
|---|-----------|-----------|----------|-----------------------------|
| Host Ni(4-MePy) ₄ (NCS) ₂ | | | | |
| Ni | 1259 (1) | 1775 (1) | 1244 (1) | 4.6 (1) |
| N(1) | 985 (4) | 1682 (3) | 616 (1) | 5.6 (2) |
| N(2) | 1592 (4) | 1928 (3) | 1873 (1) | 5.4 (2) |
| N(3) | 484 (3) | 3412 (3) | 1230 (1) | 4.9 (2) |
| N(4) | 1961 (3) | 114 (3) | 1260 (1) | 5.1 (2) |
| N(5) | 2949 (3) | 2464 (3) | 1159 (1) | 5.1 (2) |
| N(6) | -389 (4) | 1049 (3) | 1321 (1) | 4.9 (2) |
| S(1) | 1123 (3) | 1755 (2) | -220 (1) | 9.8 (1) |
| S(2) | 2243 (2) | 2077 (1) | 2702 (1) | 7.2 (1) |
| C(1) | 1032 (4) | 1712 (4) | 267 (1) | 4.9 (2) |
| C(2) | 1863 (4) | 1985 (3) | 2211 (1) | 4.7 (2) |
| C(3) | 688 (4) | 4173 (4) | 943 (1) | 5.2 (2) |
| C(4) | 188 (5) | 5229 (4) | 922 (1) | 5.7 (2) |
| C(5) | -600 (4) | 5531 (4) | 1204 (1) | 5.2 (2) |
| C(6) | -819 (4) | 4733 (4) | 1496 (1) | 5.3 (2) |
| C(7) | -265 (4) | 3711 (4) | 1500 (1) | 5.2 (2) |
| C(8) | -1163 (5) | 6661 (5) | 1196 (2) | 7.8 (2) |
| C(9) | 1494 (5) | -703 (4) | 1017 (1) | 5.5 (2) |
| C(10) | 1856 (5) | -1801 (4) | 1041 (2) | 6.0 (3) |
| C(11) | 2762 (5) | -2116 (4) | 1318 (2) | 5.9 (3) |
| C(12) | 3260 (5) | -1253 (5) | 1571 (2) | 5.8 (2) |
| C(13) | 2842 (4) | -177 (4) | 1533 (1) | 5.4 (2) |
| C(14) | 3199 (5) | -3298 (4) | 1357 (2) | 7.8 (2) |
| C(15) | 3618 (5) | 2054 (4) | 878 (2) | 5.7 (2) |
| C(16) | 4701 (5) | 2467 (5) | 815 (2) | 6.3 (3) |
| C(17) | 5145 (5) | 3340 (5) | 1052 (2) | 6.2 (3) |
| C(18) | 4459 (5) | 3776 (5) | 1344 (2) | 6.3 (3) |
| C(19) | 3394 (5) | 3326 (4) | 1385 (2) | 5.7 (3) |
| C(20) | 6370 (5) | 3829 (6) | 995 (2) | 8.5 (2) |
| C(21) | -558 (5) | 335 (4) | 1628 (1) | 5.8 (2) |
| C(22) | -1582 (5) | -206 (5) | 1674 (2) | 6.4 (3) |
| C(23) | -2506 (5) | -56 (5) | 1391 (2) | 6.2 (3) |
| C(24) | -2343 (5) | 674 (6) | 1073 (2) | 7.0 (3) |
| C(25) | -1300 (5) | 1181 (5) | 1044 (2) | 6.3 (3) |
| C(26) | -3645 (6) | -656 (6) | 1432 (2) | 9.0 (2) |
| Guest 1-MeN, molecule A | | | | |
| C(27) | 6438 (6) | 1015 (6) | 2456 (2) | 8.2 (4) |
| C(28) | 6955 (6) | 34 (5) | 2609 (2) | 7.9 (3) |
| C(29) | 8151 (7) | 65 (5) | 2750 (2) | 7.9 (3) |
| C(30) | 8771 (7) | 1022 (5) | 2751 (2) | 8.2 (3) |
| C(31) | 8939 (6) | 3084 (5) | 2623 (2) | 7.4 (3) |
| C(32) | 8373 (7) | 4008 (5) | 2486 (2) | 8.2 (4) |
| C(33) | 7196 (7) | 4016 (5) | 2334 (2) | 7.8 (3) |
| C(34) | 6592 (7) | 3105 (6) | 2318 (2) | 8.8 (4) |
| C(35) | 7122 (5) | 2025 (4) | 2470 (1) | 6.3 (2) |
| C(36) | 8255 (6) | 2044 (5) | 2616 (2) | 7.2 (3) |
| C(37) | 5210 (7) | 1031 (8) | 2295 (3) | 12.1 (5) |
| Guest 1-MeN, molecule B | | | | |
| C(38) | 4566 (7) | -2343 (8) | 350 (2) | 9.6 (5) |
| C(39) | 4341 (8) | -1248 (8) | 288 (2) | 9.7 (5) |
| C(40) | 3275 (9) | -812 (7) | 126 (2) | 10.1 (4) |
| C(41) | 2401 (7) | -1584 (7) | 10 (2) | 9.4 (4) |
| C(42) | 1682 (6) | -3548 (8) | -56 (2) | 8.7 (3) |
| C(43) | 1896 (7) | -4654 (7) | -2 (2) | 8.7 (3) |
| C(44) | 2900 (9) | -5033 (6) | 169 (2) | 8.8 (4) |
| C(45) | 3784 (7) | -4354 (7) | 283 (2) | 9.0 (4) |
| C(46) | 3668 (5) | -3159 (6) | 233 (2) | 7.4 (3) |
| C(47) | 2599 (7) | -2747 (6) | 63 (1) | 8.0 (3) |
| C(48) | 5714 (7) | -2766 (9) | 524 (3) | 12.8 (6) |

and $R_w = 0.079$. The weighting scheme was $w = 1/[\sigma^2(F) + 0.005F^2]$. Atomic parameters are listed in Table 1.*

Results and discussion

Molecular structure

Bond lengths and angles with e.s.d.'s are given in Table 2. The conformation of the host complex molecule is shown in Fig. 1 and the guest 1-MeN molecules in Fig. 2.

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and results of rigid-body thermal-motion analysis have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36259 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

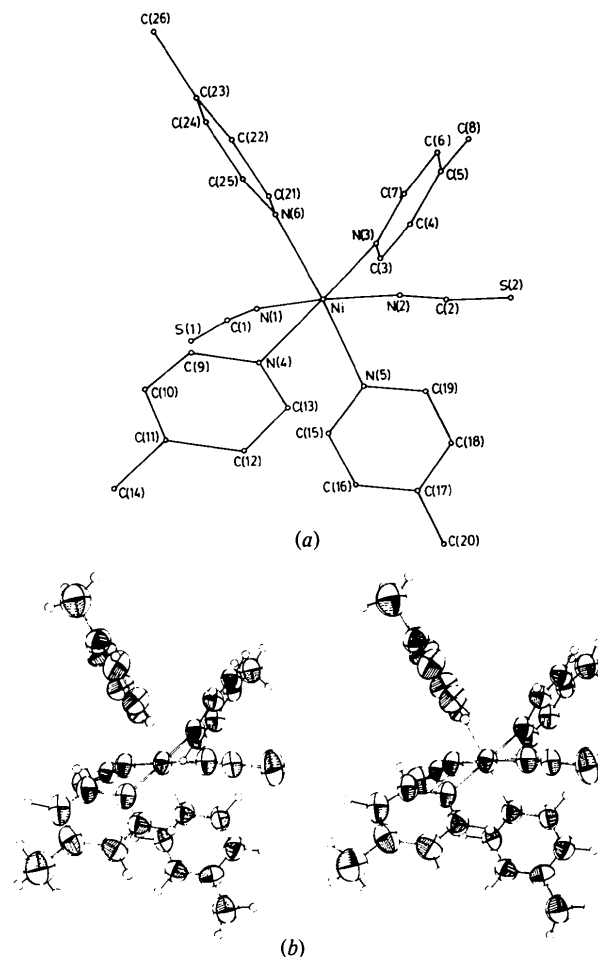


Fig. 1. The Ni(4-MePy)₄(NCS)₂ host molecule: (a) atom numbering, and (b) ORTEP (Johnson, 1965) stereoview. Ellipsoids of 50% probability are used for non-H atoms; the H atoms are indicated by spheres of 0.1 Å radii.

Table 2. Bond distances (Å), angles (°) and torsion angles (°) with *e.s.d.*'s in parentheses

The values corrected for libration are given in square brackets.

Host complex

| | | | |
|-------------|-----------|-------------|-----------|
| Ni—N(1) | 2.067 (4) | N(1)—C(1) | 1.152 (6) |
| Ni—N(2) | 2.081 (4) | N(2)—C(2) | 1.133 (6) |
| C(1)—S(1) | 1.612 (5) | | |
| C(2)—S(2) | 1.643 (5) | | |
| Ni—N(3) | 2.141 (4) | Ni—N(4) | 2.133 (4) |
| N(3)—C(3) | 1.340 (6) | N(4)—C(9) | 1.344 (6) |
| N(3)—C(7) | 1.332 (6) | N(4)—C(13) | 1.349 (6) |
| C(3)—C(4) | 1.381 (7) | C(9)—C(10) | 1.371 (7) |
| C(4)—C(5) | 1.392 (7) | C(10)—C(11) | 1.385 (8) |
| C(5)—C(6) | 1.386 (7) | C(11)—C(12) | 1.415 (7) |
| C(5)—C(8) | 1.491 (8) | C(11)—C(14) | 1.495 (7) |
| C(6)—C(7) | 1.372 (7) | C(12)—C(13) | 1.370 (7) |
| Ni—N(5) | 2.151 (4) | Ni—N(6) | 2.119 (4) |
| N(5)—C(15) | 1.338 (7) | N(6)—C(21) | 1.344 (6) |
| N(5)—C(19) | 1.345 (6) | N(6)—C(25) | 1.346 (6) |
| C(15)—C(16) | 1.372 (8) | C(21)—C(22) | 1.363 (8) |
| C(16)—C(17) | 1.373 (8) | C(22)—C(23) | 1.372 (8) |
| C(17)—C(18) | 1.388 (8) | C(23)—C(24) | 1.382 (8) |
| C(17)—C(20) | 1.551 (8) | C(23)—C(26) | 1.509 (9) |
| C(18)—C(19) | 1.355 (8) | C(24)—C(25) | 1.355 (8) |

| | | | |
|--------------------|-----------|--------------------|-----------|
| Ni—N(1)—C(1) | 167.6 (4) | Ni—N(2)—C(2) | 174.5 (4) |
| N(1)—C(1)—S(1) | 179.0 (5) | N(2)—C(2)—S(2) | 179.3 (4) |
| N(1)—Ni—N(3) | 89.7 (1) | N(1)—Ni—N(4) | 90.3 (1) |
| N(1)—Ni—N(5) | 87.9 (2) | N(1)—Ni—N(6) | 91.5 (2) |
| N(3)—C(3)—C(4) | 123.7 (5) | N(4)—C(9)—C(10) | 123.3 (5) |
| C(3)—C(4)—C(5) | 119.5 (5) | C(9)—C(10)—C(11) | 120.4 (5) |
| C(4)—C(5)—C(6) | 116.5 (4) | C(10)—C(11)—C(12) | 116.3 (5) |
| C(5)—C(6)—C(7) | 120.2 (4) | C(11)—C(12)—C(13) | 119.9 (5) |
| C(6)—C(7)—N(3) | 123.8 (4) | C(12)—C(13)—N(4) | 123.0 (4) |
| C(7)—N(3)—C(3) | 116.4 (4) | C(13)—N(4)—C(9) | 117.2 (4) |
| C(4)—C(5)—C(8) | 121.6 (5) | C(10)—C(11)—C(14) | 122.9 (5) |
| N(5)—C(15)—C(16) | 123.4 (5) | N(6)—C(21)—C(22) | 123.8 (5) |
| C(15)—C(16)—C(17) | 119.3 (5) | C(21)—C(22)—C(23) | 120.0 (5) |
| C(16)—C(17)—C(18) | 117.8 (5) | C(22)—C(23)—C(24) | 116.8 (5) |
| C(17)—C(18)—C(19) | 119.3 (5) | C(23)—C(24)—C(25) | 120.3 (5) |
| C(18)—C(19)—N(5) | 123.8 (5) | C(24)—C(25)—N(6) | 123.4 (5) |
| C(19)—N(5)—C(15) | 116.3 (4) | C(25)—N(6)—C(21) | 115.6 (4) |
| C(16)—C(17)—C(20) | 121.2 (5) | C(22)—C(23)—C(26) | 121.0 (5) |
| N(1)—Ni—N(3)—C(3) | -41 (1) | N(1)—Ni—N(4)—C(9) | -40 (1) |
| N(1)—Ni—N(5)—C(15) | -41 (1) | N(1)—Ni—N(6)—C(25) | -30 (1) |
| C(1)—N(1)—Ni—N(3) | 92 (1) | C(2)—N(2)—Ni—N(3) | -131 (1) |

Guest 1-MeN

| Molecule A | | Molecule B | |
|-------------------|------------|-------------------|------------|
| C(27)—C(28) | 1.387 (9) | C(38)—C(39) | 1.340 (13) |
| C(27)—C(35) | 1.435 (9) | C(38)—C(46) | 1.450 (11) |
| C(28)—C(29) | 1.422 (10) | C(39)—C(40) | 1.402 (13) |
| C(29)—C(30) | 1.344 (9) | C(40)—C(41) | 1.395 (12) |
| C(30)—C(36) | 1.410 (9) | C(41)—C(47) | 1.410 (11) |
| C(31)—C(36) | 1.466 (9) | C(42)—C(47) | 1.455 (10) |
| C(31)—C(32) | 1.338 (9) | C(42)—C(43) | 1.347 (12) |
| C(32)—C(33) | 1.410 (11) | C(43)—C(44) | 1.327 (11) |
| C(33)—C(34) | 1.287 (10) | C(44)—C(45) | 1.332 (11) |
| C(34)—C(35) | 1.492 (9) | C(45)—C(46) | 1.435 (11) |
| C(35)—C(36) | 1.358 (9) | C(46)—C(47) | 1.403 (9) |
| C(27)—C(37) | 1.474 (10) | C(38)—C(48) | 1.489 (11) |
| C(27)—C(28)—C(29) | 118.4 (6) | C(38)—C(39)—C(40) | 124.9 (8) |
| C(28)—C(29)—C(30) | 121.7 (6) | C(39)—C(40)—C(41) | 117.1 (8) |
| C(29)—C(30)—C(36) | 121.1 (7) | C(40)—C(41)—C(47) | 120.3 (7) |
| C(30)—C(36)—C(35) | 118.0 (6) | C(41)—C(47)—C(46) | 121.4 (7) |
| C(36)—C(35)—C(27) | 122.5 (5) | C(47)—C(46)—C(38) | 117.4 (7) |
| C(35)—C(27)—C(28) | 118.2 (6) | C(46)—C(38)—C(39) | 118.9 (7) |
| C(31)—C(32)—C(33) | 123.8 (6) | C(42)—C(43)—C(44) | 122.2 (7) |
| C(32)—C(33)—C(34) | 120.8 (6) | C(43)—C(44)—C(45) | 122.6 (8) |
| C(33)—C(34)—C(35) | 120.3 (7) | C(44)—C(45)—C(46) | 120.3 (7) |
| C(34)—C(35)—C(36) | 117.6 (5) | C(45)—C(46)—C(47) | 117.6 (6) |
| C(35)—C(36)—C(31) | 121.5 (5) | C(46)—C(47)—C(42) | 118.5 (6) |
| C(36)—C(31)—C(32) | 116.1 (6) | C(47)—C(42)—C(43) | 118.8 (6) |
| C(35)—C(27)—C(37) | 120.7 (6) | C(46)—C(38)—C(48) | 118.2 (8) |

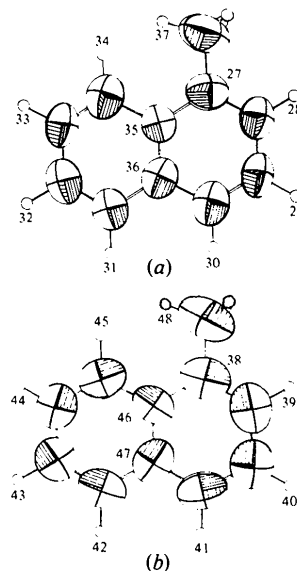


Fig. 2. An ORTEP plot of (a) 1-MeN molecule A and (b) 1-MeN molecule B guest molecules. Ellipsoids of 50% probability are used for C atoms; H atoms are represented by circles of 0.1 Å radii. Numbers shown denote the numbering of the C and H atoms.

The host molecule is propeller shaped and its geometry differs significantly from that found in the tetragonal β -phase of $\text{Ni}(4\text{-MePy})_4(\text{NCS})_2$ (Andreotti, Bocelli & Sgarabotto, 1972; de Gil & Kerr, 1977) or in triclinic clathrates of the complex (Lipkowski, Sgarabotto & Andreotti, 1980). In the structures mentioned above, the $\text{Ni}(4\text{-MePy})_4(\text{NCS})_2$ molecule adopts C_2 and C_i symmetry respectively. In the clathrate described here the complex is asymmetric. The asymmetry is more pronounced than that of the complex in its non-clathrated ' α -phase' (Kerr & Williams, 1977). In particular, the difference between the Ni—N(5) and Ni—N(6) distances (0.032 Å) seems to be significant and the N(1)—Ni—N(5) angle

Table 3. Comparison of N—C and Ni—N bond lengths and Ni—N—C bond angles in isothiocyanate ligands

| Clathrate with (guest compound) | Ni—N—C(S) (°) | Ni—N(CS) (Å) | N—C (Å) | C—S (Å) | Reference |
|---------------------------------|---------------|--------------|------------|------------|-----------|
| 1-MeN | 167.6 (4) | 2.066 (4) | 1.151 (6) | 1.614 (5) | (a) |
| | 174.5 (4) | 2.082 (4) | 1.333 (6) | 1.644 (5) | (a) |
| 2-MeN | 169.0 (4) | 2.046 (2) | 1.149 (2) | 1.624 (2) | (b) |
| 2-BrN | 170.3 (12) | 2.029 (7) | 1.144 (8) | 1.610 (7) | (b) |
| Methanol | 158.1 (6) | 2.070 (7) | 1.137 (9) | 1.623 (10) | (c) |
| p-Xylene | 163.0 (7) | 2.061 (7) | 1.135 (11) | 1.617 (9) | (c) |
| m-Xylene | 165.1 (4) | 2.068 (4) | 1.134 (6) | 1.623 (5) | (c) |
| Nonclathrated 'α-form' | 163.5 (5) | 2.066 (4) | 1.136 (6) | 1.629 (5) | (d) |
| | 156.7 (4) | 2.070 (4) | 1.128 (7) | 1.639 (6) | (d) |

References: (a) Present study; (b) Lipkowski *et al.* (1980); (c) Lipkowski *et al.* (1981); (d) Kerr & Williams (1977).

Table 4. *Least-squares planes and atomic deviations* (Å)

Atoms marked with asterisks were not included in the least-squares calculations.

| | | | |
|---|------------|--------|------------|
| (I) $1.2114X + 0.8353Y + 32.2400Z = 4.3044$ | | | |
| N(3) | 0.005 (3) | N(5) | -0.005 (3) |
| N(4) | 0.005 (3) | N(6) | -0.005 (3) |
| Ni* | 0.007 | | |
| (II) $10.5243X + 4.6568Y - 5.9966Z = 1.4057$ | | | |
| N(1) | 0.045 (3) | N(3) | -0.045 (3) |
| N(2) | 0.045 (3) | N(4) | -0.044 (3) |
| Ni* | 0.000 | | |
| (III) $-4.6143X + 10.8912Y + 0.0931Z = 1.3584$ | | | |
| N(1) | 0.025 (3) | N(5) | -0.025 (3) |
| N(2) | 0.024 (3) | N(6) | -0.024 (3) |
| Ni* | 0.005 | | |
| (IV) $8.1830X + 4.3926Y + 17.9065Z = 4.0942$ | | | |
| N(3) | 0.003 (3) | C(6) | -0.007 (3) |
| C(3) | -0.010 (4) | C(7) | 0.005 (4) |
| C(4) | 0.008 (3) | C(8)* | 0.022 |
| C(5) | 0.000 (3) | Ni* | -0.057 |
| (V) $8.1897X + 2.2993Y - 23.9105Z = -1.3771$ | | | |
| N(4) | -0.003 (3) | C(12) | 0.003 (4) |
| C(9) | 0.007 (4) | C(13) | -0.002 (3) |
| C(10) | -0.006 (4) | C(14)* | -0.006 |
| C(11) | 0.001 (3) | Ni* | -0.158 |
| (VI) $4.1161X - 7.7280Y + 21.1026Z = 1.7530$ | | | |
| N(5) | 0.003 (3) | C(18) | 0.001 (3) |
| C(15) | 0.002 (4) | C(19) | 0.004 (3) |
| C(16) | -0.005 (3) | C(20)* | 0.010 |
| C(17) | 0.004 (4) | Ni* | 0.019 |
| (VII) $-4.0814X + 9.1082Y + 18.4440Z = 3.5417$ | | | |
| N(6) | 0.009 (4) | C(24) | 0.008 (4) |
| C(21) | -0.006 (4) | C(25) | 0.010 (4) |
| C(22) | 0.004 (4) | C(26)* | 0.010 |
| C(23) | -0.004 (3) | Ni* | -0.144 |
| (VIII) $-3.9800X + 2.3205Y + 30.9204Z = 5.2741$ | | | |
| C(27) | -0.007 (5) | C(33) | 0.011 (6) |
| C(28) | 0.033 (6) | C(34) | -0.010 (6) |
| C(29) | 0.000 (6) | C(35) | -0.001 (5) |
| C(30) | -0.022 (5) | C(36) | 0.004 (6) |
| C(31) | -0.006 (4) | C(37) | -0.012 (7) |
| C(32) | 0.010 (6) | | |
| (IX) $-4.6078X + 0.7110Y + 30.9456Z = -1.1918$ | | | |
| C(38) | 0.004 (6) | C(44) | 0.021 (6) |
| C(39) | -0.006 (6) | C(45) | 0.014 (6) |
| C(40) | 0.015 (5) | C(46) | -0.002 (5) |
| C(41) | 0.004 (6) | C(47) | -0.006 (7) |
| C(42) | -0.009 (5) | C(48) | -0.016 (6) |
| C(43) | -0.019 (6) | | |

Table 4 (cont.)

Dihedral angles (°)

| | | | |
|--------------|-----------|------------|-----------|
| (I)-(II) | 89.5 (5) | (I)-(IV) | 45.9 (7) |
| (I)-(III) | 90.3 (5) | (I)-(V) | 54.3 (7) |
| (II)-(III) | 90.2 (5) | (I)-(VI) | 48.9 (6) |
| (VIII)-(IX) | 8.4 (18) | (I)-(VII) | 56.7 (7) |
| (IV)-(VIII) | 67.8 (10) | (IV)-(IX) | 73.3 (11) |
| (V)-(VIII) | 34.0 (10) | (V)-(IX) | 27.0 (13) |
| (VI)-(VIII) | 68.6 (10) | (VI)-(IX) | 64.4 (12) |
| (VII)-(VIII) | 40.2 (12) | (VII)-(IX) | 47.3 (10) |

[87.9 (2)°] differs significantly from 90°. The angles at the thiocyanate N atoms are rather larger here [167.6 (4) and 174.5 (4)°] than in the α -phase (156.7 and 163.5°). The conformation of the thiocyanate groups about the Ni-N bonds is highly asymmetric, torsion angles C(1)-N(1)-Ni-N(3) and C(2)-N(2)-Ni-N(3) being 92(1) and -131(1)°.

It seems clear, on the basis of the data listed in Table 3, that differences in the Ni-N-C(S) bond angles observed in Ni(4-MePy)₄(NCS)₂ molecules in different crystal structures cannot be ascribed to any electronic effect and should be interpreted in terms of molecular packing. A similar conclusion has recently been drawn by Hartl & Brüdgam (1980) from studies on Co(C₅H₅N)₄(NCS)₂ and its molecular adducts. It is thus reasonable to assume that both the conformation of the isothiocyanate groups about the Ni-N(CS) bonds, and the Ni-N-C(S) bond angles reported herein are a result of crystal packing forces, a range of ca 150-180° being permissible for Ni-N-C(S) bond angles (Müller, 1977).

The four N atoms of the MePy groups and Ni are coplanar (Table 4). As in the α phase, the pyridine rings are planar to within 0.01 Å and the Ni atom deviates from these planes significantly. The dihedral angles between the pyridine rings and the N(3), N(4), N(5), N(6) plane range from 45.9 to 56.7°. These values are about 5° lower than the corresponding angles in the α phase and about 3° lower than in the β phase.

The conformation of the four MePy ligands about their Ni-N coordination bonds is fairly close to the optimum geometry found for this system from non-bonded energy calculations (Lipkowski, 1981).

Thermal motion

The thermal motion of the 4-MePy ligands and the 1-MeN guest molecules has been analysed in terms of rigid-body motion (Schomaker & Trueblood, 1968). The resulting corrections to bond lengths within the rigid groups are included in Table 2. The r.m.s. amplitudes of vibration of both 1-MeN molecules are equal within the error limits. Libration is highly anisotropic. Translational motions have, for both guest molecules, r.m.s. amplitudes of about 0.32 Å in

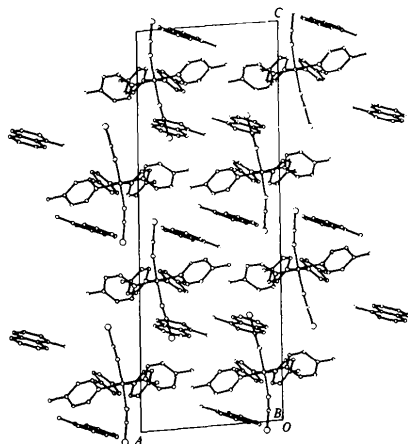


Fig. 3 The packing of the molecules viewed along [010].

directions not much different from **a** and **b** and significantly lower values, 0.22 Å, in the direction close to **c**. Detailed results of the thermal-motion analysis of the 1-MeN molecules have been deposited.*

Packing

The molecular packing, which is illustrated by a projection along [010] (Fig. 3), is of a layer-type. Discrete $\text{Ni}(4\text{-MePy})_4(\text{NCS})_2$ molecules form layers perpendicular to **c** at $z = \frac{1}{8}, \frac{3}{8}, \frac{5}{8}$ and $\frac{7}{8}$. Isothiocyanate groups penetrate the space between these layers and subdivide it into cavities. Asymmetric host $\text{Ni}(4\text{-MePy})_4(\text{NCS})_2$ molecules border two symmetrically independent layers of guest molecules. At $z = 0$ and $\frac{1}{2}$ the layers consist of centrosymmetrically related guest molecules **B**, while at $z = \frac{1}{4}$ and $\frac{3}{4}$, molecules **A** are related by the 2_1 symmetry.

The molecular packing differs greatly from that found in the 2-MeN clathrate (Lipkowski, Sgarabotto & Andreotti, 1980), although both involve a layer-like type of packing. Closest intermolecular contacts are given in Table 5.

Conclusion

As stated in the introduction the 1-MeN clathrate is thermodynamically more stable than the 2-MeN clathrate. However, comparison of molar volumes (676×10^{-6} and $650 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ for the 1-MeN and 2-MeN clathrate respectively) indicates significantly more effective packing in the less stable crystalline phase. It seems that the reason for the above difference in thermodynamic stability (and thus the reason for clathration selectivity in this system) could be the difference in intramolecular, non-bonded energy of the host. In the 2-MeN clathrate close packing is achieved

* See deposition footnote.

Table 5. Closest intermolecular contacts (Å)

| Host-host | | $r_1 + r_2^*$ |
|----------------------------------|------------|---------------|
| S(2) ... H(C22) ^(g) | 2.944 (4) | 3.05 |
| H(C4) ... H(C10) ^(c) | 2.431 (7) | 2.40 |
| H(C8) ... H(C10) ^(c) | 2.441 (7) | |
| Host-guest molecule A | | |
| S(2) ... H(C33) ^(e) | 2.922 (5) | 3.05 |
| S(2) ... H(C32) ^(e) | 3.023 (5) | |
| S(2) ... H(C31) ^(b) | 3.047 (5) | |
| H(C6) ... C(32) ^(b) | 2.756 (7) | 2.90 |
| H(C26) ... C(37) ^(b) | 2.767 (7) | |
| C(2) ... H(C29) ^(g) | 2.795 (9) | |
| C(6) ... H(C30) ^(g) | 2.826 (8) | |
| C(7) ... H(C29) ^(g) | 2.864 (8) | |
| H(C6) ... C(33) ^(b) | 2.867 (8) | |
| H(C22) ... C(29) ^(b) | 2.884 (8) | |
| C(2) ... H(C32) ^(e) | 2.907 (7) | |
| H(C14) ... C(28) ^(e) | 2.928 (11) | |
| H(C14) ... C(29) ^(e) | 2.937 (11) | |
| H(C14) ... C(35) ^(e) | 2.955 (12) | |
| H(C14) ... C(30) ^(e) | 2.968 (11) | |
| H(C14) ... C(36) ^(e) | 2.969 (11) | |
| H(C14) ... C(27) ^(e) | 2.971 (12) | |
| H(C26) ... H(C37) ^(a) | 2.431 (14) | |
| Host-guest molecule B | | |
| S(1) ... H(C48) ^(d) | 3.031 (5) | 3.05 |
| H(C26) ... H(C48) ^(a) | 2.429 (12) | 2.40 |
| H(C3) ... C(44) ^(c) | 2.953 (8) | 2.90 |
| H(C4) ... C(43) ^(c) | 3.005 (9) | |
| C(1) ... H(C42) ^(h) | 2.837 (8) | |

Symmetry codes: (a) $1 + x, y, z$; (b) $x - 1, y, z$; (c) $x, 1 + y, z$; (d) $1 - x, y, z$; (e) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (f) $-x, \frac{1}{2} + y, \frac{3}{2} - z$; (g) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (h) $-x, -y, -z$.

* Sum of van der Waals radii.

by imposing a centrosymmetric conformation on the host complex which involves significant repulsive interactions (Lipkowski, 1981), which is not observed in the structure reported here.

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Orthorhombic and Monoclinic Allotropes of *cis*-[PtCl₂(PMePh₂)₂], *cis*-Dichlorobis(methyldiphenylphosphine)platinum(II): Structure Analyses

BY HO KIN-CHEE, GEORGE M. MCLAUGHLIN, MARY MCPARTLIN* AND GLEN B. ROBERTSON

Research School of Chemistry, The Australian National University, Canberra, ACT, Australia

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Abstract

The crystal-structure analysis of two stable allotropes of *cis*-[PtCl₂(PMePh₂)₂] (C₂₆H₂₆Cl₂P₂Pt, *M_r* = 666.44) is reported. (I) is orthorhombic, space group *P*2₁2₁2₁ with *a* = 10.0271 (6), *b* = 14.5578 (6), *c* = 17.0528 (8) Å, *Z* = 4, *V* = 2489.24 Å³, *D_m* = 1.77 (2), *D_c* = 1.778 Mg m⁻³, *F*(000) = 1296, *μ*(Cu Kα) = 14.025 mm⁻¹, *T* = 294 (1) K. (II) is monoclinic, space group *P*2₁/*c* with *a* = 12.8639 (9), *b* = 13.6580 (3), *c* = 18.9963 (14) Å, *β* = 131.312 (6)°, *Z* = 4, *V* = 2506.93 Å³, *D_m* = 1.76 (1), *D_c* = 1.766 Mg m⁻³, *F*(000) = 1296, *μ*(Cu Kα) = 13.926 mm⁻¹, *T* = 294 (1) K. Full-matrix least-squares refinements, with fixed H atoms, converged with *R* = 0.024 for (I) (2296 reflections) and 0.019 for (II) (3220 reflections). Molecules in both allotropes are essentially *cis* square planar, with similar small tetrahedral deformations of the coordination spheres. In (II) the PMePh₂ ligands are disposed less symmetrically than in (I), resulting in inequivalence of the Cl–Pt–P angles [90.77 (4) and 83.43 (4)°] and of the Pt–Cl distances [2.359 (1) and 2.345 (1) Å]. The Pt–P distances are equivalent within experimental error [mean 2.245 (1) Å]. Corresponding mean bond distances for (I) are Pt–P, 2.249 (1) and Pt–Cl, 2.350 (1) Å.

Introduction

In the course of attempting to recrystallize *trans*-[PtCl(COCH₃)(PMePh₂)₂] from chlorinated solvents,

excellent crystals (I) exhibiting well-defined *mmm* symmetry were obtained from ethanol/chloroform solution. The discrepancy between the observed density [1.77 (2) Mg m⁻³, measured by flotation in aqueous BaI₂] and that calculated for the above formulation (1.798 Mg m⁻³) was larger than expected, but consistent with imperfect wetting. Accordingly, the discrepancy was ignored and diffraction data were collected with these crystals. Subsequent solution of the structure showed the product to be *cis*-[PtCl₂(PMePh₂)₂]. Since the detailed structure of this molecule permits some quantification of the *trans* influence of the PMePh₂ ligand (on Pt–Cl bond distances) refinement of the structure was continued. Attempts to obtain crystals of the acyl complex were also continued. An apparently successful recrystallization from C₆H₆/EtOH/*n*-hexane under rigorously dry conditions yielded well-formed crystals (II) with *2/m* symmetry. Observed and calculated densities were in excellent agreement (apparently) and, hence, a second set of data was collected on the assumption that this time we had the acyl complex. It was, in fact, a second crystalline modification of *cis*-[PtCl₂(PMePh₂)₂] and the density agreement was traced to a numerical error. However, despite being derived from a common precursor, *trans*-[PtCl(COCH₃)(PMePh₂)₂], and both having the *cis* conformation at Pt, molecules in (I) and (II) exhibit distinct conformational differences. Therefore, it seemed worthwhile to refine (II) to convergence also, with a view to investigating the effects of the conformational differences on metal–ligand bond lengths and angles.

* Present address: Department of Chemistry, The Polytechnic of North London, Holloway, London N7 8DB, England.